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Beamline X14A: Multi-Energy X-ray Holography (MEXH) is a new technique for directly imaging atomic structures in the bulk or at surfaces of solids. The figure is a holographic reconstruction of an iron (0,0,1) layer in a natural slab of Hematite, (Fe_2O_3) which consists of alternating layers of iron and oxygen. [T. Gog (ORNL), P.M. Len, C.S. Fadley (UC Davis), D. Bahr, C. Sanchez-Hanke, G. Materlik (HASYLAB)] See also the X14A experimental summaries in the "Abstracts" section of this book.

ONE **INTRODUCTION**

NSLS

INTRODUCTION

Michael Hart
NSLS Chairman

Another lean year, in which the budget remained level in at year dollars but fell in real terms. Nevertheless we saw a high level of scientific activity and facility development and improvement. The end of the Fiscal Year (FY 1995) brought substantial changes to the staff of the NSLS. It became necessary to solicit volunteers for a reduction in staff so as to allow for a redirection of funds into areas considered vital to improve research operations. Many years of experience were lost when Arie van Steenberg, George Stenby, Bob Larson, Ken Batchelor, Norman Fewell, Paul LeDoux and Clem Auguste volunteered to take retirement. The year ended with the certainty that FY 1996 would be the year in which the Scientific Facilities Initiative would be funded.

Highlights and themes of the science program are summarized in articles by NSLS staff and users, providing an overview which displays the evidence of extreme diversity and high quality. The detailed publication lists and user's reports are described in later pages and in over 700 publications in the journal literature.

During the year, in the March 1995 Newsletter, the concept of Beamline Confederations was first explored and this continues to be an important aspect of the future at NSLS for users and staff alike. In the present economic climate it has become increasingly difficult to obtain the necessary funds to ensure year round operations for all the beamlines. An increase in scale, through co-operation, collaboration and correlation of planning and investment could enable PRTs to achieve more than each would achieve alone. In areas such as Powder Diffraction, Structural Biology, X-ray Absorption Spectroscopy, and Reflectometry several beamlines exist at NSLS. In each case there are benefits to be won, through combined R & D in both soft-ware and hardware, through the common provision of spares and through the enhanced intellectual resources of a wider community. In some of these examples the combination of interest and expertise in the application of neutron probes is also of importance.

The Structural Biology Addition was formally Dedicated on 10 May 1995 when Roland Hirsch from the DOE Office of Health & Environmental Research was

joined by BNL Laboratory Director Nicholas Samios, Denis McWhan (BNL Associate Director for Basic Energy Sciences) and William Studier, BNL Biology Department Chairman for a ceremonial ribbon cutting. Funds for this key development of user laboratory space included the DOE Office of Health & Environmental Research, BNL General Plant Project Funds (GPP), the Howard Hughes Medical Institute, Exxon and New York State University at Stony Brook. At the end of the year the users took possession of the laboratory space and the NSLS control room and ES&H staff planned to move too.

A Department of Energy Customer Satisfaction Survey was conducted by an experienced contractor under the direction of the DOE Task Force on the Science and Technology (S & T) business line. The NSLS provided the DOE with a contact list of users for the purpose of random polling, and extensive questionnaires were also completed by PRT members and by the Users' Executive Committee. 80% of the customers of the S & T reported that they were "satisfied" or "very satisfied".

Yet another successful year of machine improvements and operations was achieved; the energy of the VUV ring was increased to 800 MeV resulting in longer lifetime and a 30% increase in integrated current and plans were made to increase the booster energy to track that of the ring. Further improvements include the first demonstration of "top off" mode in which quasi-continuous injection keeps the current near its maximum value and so reduces the effects of thermal cycling on beam line optics while maximizing the integrated current. On the X-ray ring maximum current operation was increased to 300 mA and the Thermal Limits Task Force set out a plan for eventual running at up to 438 mA at 2.584 GeV or 250

mA at 2.8 GeV after the replacement of the 34 Beryllium windows which presently limit such operating conditions.

Early in the year the Elliptically Polarized Wiggler was installed and tested in the X-13 R & D straight section of the X-Ray Ring. The modified Prototype Small Gap Undulator was reinstalled and operated at a 5.6 mm magnet gap (2.5 mm electron beam gap) to provide 2.5 keV X-rays in the fundamental and 7.5 keV X-rays in the third harmonic with a partial lifetime contribution of only 36 hours. The Accelerator Test Facility provided access to 15 currently approved experiments including the first demonstration of Inverse FEL acceleration of electrons, the observation of micro-bunching and the development of slice-emittance techniques for beam diagnostics. The NSLS hosted the 17th International Free Electron Laser Conference, an important meeting both in terms of content and timing in the definition of the next few years R & D towards fourth generation synchrotron radiation sources.

A very productive year for our staff and users.

NSLS

ENVIRONMENT, SAFETY AND HEALTH UPDATE

William Thomlinson
Associate Chairman
NSLS

The ES&H activities at the NSLS during FY95 focused on the implementation of old and new programs, getting prepared for the coming of the new Personnel Radiation Protection law on January 1, 1996, and adjusting to several significant personnel changes.

It is perhaps the personnel changes which are the most important issue which we faced. At the end of FY95, we lost the services of our ES&H Coordinator, Kenneth Batchelor, our Quality Assurance Representative, Paul LeDoux, and our Safety Associate, Clement Auguste. It is never easy to lose so many people at one time, especially since some of them were key, highly experienced personnel on whom we had relied for many years. During this last year under the direction of Ken Batchelor, the NSLS finally achieved formal classification by DOE as a low hazard accelerator. That means that the DOE orders and guidelines which pertain to our operations are now clarified. Previously we had operated under the assumption that we would be low hazard, but we needed final approval.

We have been very fortunate in being able to fill these openings with extremely qualified personnel who have already been putting their marks on the positions. The central position of ES&H Coordinator has been filled by Nicholas Gmür who has extensive experience with safety issues regarding the medical research programs and as ALARA (As Low As Reasonably Achievable) Coordinator for the NSLS. It has already been a busy time since the new Radiation Protection Program, Federal Code 10CFR835, kicks in January 1, 1996 and we have had to undergo reviews, revise many of our existing SEAPPMs (Safety and Environmental Administrative Policy and Procedure Manual), and write many new ones.

The transition has been smooth and we are now pretty much up to speed. The position of ALARA Coordinator has been assumed by William Thomlinson, replacing Nicholas Gmür. Under the policies of 10CFR835, ALARA is much more formally recognized and mandated, so we have been busy naming new members to replace those who have left the Laboratory.

It has long been felt that ES&H should be an integrated concept at the NSLS, and the change of our QA Representative from Paul LeDoux to Dennis Klein has provided the perfect opportunity. Dennis Klein comes to the position from an extensive technical background and also as the NSLS Training Coordinator. We have thus been able to combine training and QA in a single office, reporting formally to both the ES&H Associate Chairman and to the Assistant to the Chairman for Administration.

John Aloï has moved from his Operations Coordinator role to become a Staff Engineer in our group. The timeliness of this move cannot be underestimated. John is already giving the necessary attention to critical matters which had been neglected or not initiated. The arrival of these three individuals, working with Thomas Dickinson, our Safety Officer, Andrew Ackerman, our Safety Engineer, and our S&EP representatives (Chris Weilandics, Rudy Zantopp and Eric Seebeck), ensures that we will be able to maintain our strong ES&H program.

Most of the preparation for the start of the new Personnel Radiation Protection Program has centered around updating our SEAPPMs. The NSLS is in very good shape with regard to the new federal code since we have always maintained a strong safety and ES&H effort. The NSLS is proud of its record in, for example, user safety; communication to staff and users on essential safety issues, the formalizing of our ALARA program, reporting of off-normal events, and training. A recent review by BNL of our preparations for 10CFR835 showed only a few minor areas that will need attention.

The attention of the ALARA Committee this year was focused on obtaining reliable data on the radiation levels in offices in the NSLS which come from operation of the booster and the VUV Ring. The data is now reliable enough to plan for reducing the levels through various shielding measures. These measures will be in addition to those taken in the past several years which have reduced the levels in all but a few offices to below NSLS administrative levels. There was some progress in removing

radiological warning signs around the facility due both to decreased levels after shielding upgrades and changes in the administrative policies for posting. The Committee is working toward the goal of having all radiation warning signs on office doors eliminated. There is much work yet to be done.

The Electrical Safety Review of the NSLS Experimental Areas has been completed by Michael Buckley, John Aloï and Steve Kemp. This review was an intensive study of each beamline to determine what short term critical electrical hazards exist and what longer term, non-immediate problems exist. There were many minor immediate problems found which are to be addressed by the beamline personnel. A study is now underway to address the larger, man-power intensive and costly issues (e.g., moving circuit breaker panels which do not meet access requirements). It is expected that the NSLS will share in the responsibility for correcting these deficiencies, using BNL and NSLS staff and resources. We hope to have completed this project by the end of FY96. Joe Sheehan, Electrical Engineer, is carrying out a similar review for the remainder of the NSLS technical space.

Off-normal events, and the reporting of those events to DOE, are taken very seriously by the NSLS. We have historically had very few reportable events, a record which is due to our highly trained and professional staff, coupled with our trained and concerned user population. However, occasionally we do have such events and this year was no exception. Fortunately, none of the events resulted in injury to personnel, but in at least one case of violation of electrical safety (lock-out, tag-out) procedures, the potential existed. By following through on the reports and lessons learned from these events, the NSLS is attempting to become a safer environment in which to work. In the case of the electrical safety event, intensive re-training of cognizant staff followed, the SEAPPM covering lock-out, tag-out procedures was revised and it was clearly stated once again that safety on the job is the first priority for all staff members and guests. In other events, more clarity of administrative and interlock procedures has been necessary, followed by the issuing of policies and additional training.

NSLS

USERS' EXECUTIVE COMMITTEE

Paul Zschack

Oak Ridge National Laboratory

UEC Chair

The Users' Executive Committee (UEC) continues to serve as a primary communication vehicle between the User community and the NSLS Administration. Representing the User Association, the UEC hosted four Town Meetings during 1995 to facilitate useful interaction between the NSLS staff and NSLS users. Following each Town Meeting, the UEC met with the NSLS management and the BNL Directorate to further discuss relevant issues. I extend sincere thanks to the UEC Membership, the NSLS staff and management, the BNL Directorate, and all other volunteers who took active roles in continuing the UEC mission throughout the last year.

In addition to advocacy for user quality-of-life issues, the UEC has taken initiative and sanctioned a study panel to evaluate the current health of the PRTs and General User programs. Geraldine Lamble (NSLS), Jean Jordon-Sweet (IBM), and Robert Sweet (BNL - Biology) have spearheaded this effort. Results of this in-depth study will be used to aid planning for the future, and a final report with specific recommendations has by now been provided to the NSLS Chairman.

It has never been more important for users of the NSLS and NSLS staff and management to work together to find solutions to the problems facing many research efforts at the NSLS. I believe we all recognize the need to be more creative to get more accomplished with fewer resources. One way to accomplish this is through economies of scale brought about by beamline confederations or consortia. In one form or another, these will certainly be a part of our future.

An example of the advantages of coordinated activities on a larger scale is the success of the Science Facilities Initiative in the BES budget. Hard work by the DOE and Facility Directors, and grass roots support from users was rewarded by an increase in the Basic Energy Sciences budget targeted for the National User Facilities. A portion of these funds have been made available to individuals for "...new capabilities or for upgrading existing research capabilities...at DOE-supported synchrotron facilities..." I am confident many outstanding proposals

have been submitted by NSLS users to the DOE for this grant support. We can also be hopeful that this Initiative results in a long-term increase in funding for synchrotron radiation research and is not simply a bump on the funding profile.

The Scientific Program Support Committee (SPSC) remains as a standing subcommittee of the UEC and continues to provide a leading role in advocating the users' position on many technical and quality of life issues within the NSLS. Lars Furenlid (NSLS) and Mike Sansone (Exxon) currently co-chair the SPSC, which has become involved in safety and compliance issues such as the DOE chemical tracking. The SPSC continues to be a most effective body in support of user issues.

The Annual Users' Meeting is the most visible function sponsored by the UEC. In addition to invited talks and a successful poster session, a satellite workshop on XAFS was held. This permitted users attending the Annual Meeting and traditional Workshops to also participate in the XAFS program. The popularity of the workshop programs has inspired a change for next year's annual meeting. To offer wider participation in the workshops, the program will be split into 2 days, providing the opportunity to attend 2 one-day workshops. The keynote address at the Annual Meeting was given by Robert Galvin, Chairman of the Executive Board of Motorola, Inc., and Chairman of the Task Force on Alternative Futures for the DOE National Labs. Mr. Galvin provided an eloquent and provocative opinion of the future of scientific research at the National Labs. Going beyond the Task Force Report, privatization is seen as the eventual form of the National research facilities. Not all users agree with Mr. Galvin's assessment, but this address certainly inspired much lively discussion. New to the 1995 meeting was the recognition of a Distinguished User to acknowledge the research efforts of an NSLS investigator. The inaugural Distinguished User was Cullie J. Sparks of the Oak Ridge National Lab whose contributions to synchrotron radiation research include work in focusing optics, diffuse x-ray scattering, and

**Users' Executive Committee and
Special Interest Group Representatives**

(Front, from left to right)

Paul Zschack (ORNL), Stephan Ginell (ANL), Michael Dudley (SUNY - Stony Brook), Eva Rothman (NSLS), Sue Wirik (SUNY - Stony Brook), and Peter Stephens (SUNY-Stony Brook).

(Back, from left to right, standing)

Kim Mohanty (BNL-Physics), Dan Fischer (NIST), David Hanson (SUNY - Stony Brook), Jean Jordan-Sweet (IBM), Doon Gibbs (BNL-Physics), Jon Levin (U. of Tennessee), Kevin Smith (Boston U.), Boris Sinkovic (New York U.), Syed Qadri (NRL), and Craig Thorn (BNL-Physics).

Absent from photo are Simon Bare (Dow Chemical), and David Johnson (Old Dominion U.).

anomalous scattering techniques. Cullie also served as the Chairman of the second UEC back in the early 1980s. The conference banquet was held at the Port Jefferson Country Club, and was well attended. Finally, we saw evidence that the user community continues to expand as a new Special Interest Group (SpIG) in Biological Scattering was formed. The overwhelming approval from the meeting attendees is indication that new research areas are very well received at the NSLS. I suspect the biology community will continue to be an important segment of

the NSLS User population in the future. The success of the Annual Meeting is primarily due to the hard work of the organizing committee. I am grateful to Steven Ehrlich, Linda Feierabend, Dan Fischer, Eva Rothman, and Sue Wirick for all their hard work and effort.

Sometimes we take for granted just how easy it is to work effectively at the NSLS. The hard work of past UEC committees, past NSLS Chairpersons, the NSLS User Administration Office, the NSLS staff, and the BNL Directorate should be acknowledged.

Beamline X4A and X25: The structure of a specific complex between the p50 subunit of the transcription factor NF κ B and DNA was solved. Two orthogonal views of this complex are shown. The p50 protein (365 amino-acid residues in the form shown here) binds to DNA as a dimer. Its polypeptide chain (represented as a ribbon) folds into two domains (colored yellow and red). The amino-terminal domain (yellow) contains most of the segments that interact specifically with DNA; the carboxy-terminal domain (red) mediates dimerization. The DNA (blue) contains 11 base pairs. [C.W. Muller, F.A. Rey, M. Sodeoka, G.L. Verdine, and S.C. Harrison (Howard Hughes Medical Institute and Harvard University); reported in *Nature* 373, 311-317 (1995)]

TWO SCIENTIFIC DISCIPLINES

SCIENCE

ATOMIC AND MOLECULAR SCIENCE

Mei-Ling Shek
NSLS

I. VALENCE ELECTRONIC EXCITATION

The thrust of the gas phase research on beamline U11 is discharge flow-photoionization mass spectrometry. From the photoionization efficiency spectra of HOI and IO, the adiabatic ionization energies have been determined, for the first time, for HOI (X^1A') $\rightarrow$ HOI⁺ (X^2A'') and IO ($X^2\Pi_{3/2}$) $\rightarrow$ IO⁺ ($X^3\Sigma^-$). In addition to the vibrational structure of the cation, the photoionization of IO also displays autoionization features correlated with Rydberg excitations, as shown in Figure 1.

II. INNER-SHELL EXCITATION

On beamline U13UA, Auger and resonance Auger spectra of methane are obtained as the basis of understanding the highly excited valence states of singly and doubly charged molecular ions due to core hole excitations in hydrocarbons. Figure 2 shows the Auger spectrum of methane following C 1s photoionization, as well as the resonance Auger spectra due to C 1s $\rightarrow$ 3s and 1s $\rightarrow$ 3p excitations, at chosen photon energies based on the total ion yield spectrum. The shifts towards higher electron kinetic energies in the resonance Auger spectra are consistent with the interpretation of de-excitation of Rydberg states to 2-hole-1-electron valence final states.

The dynamics of core hole excitation and de-excitation phenomena are also of great interest on beamline X1B. The feasibility of measuring threshold photoelectrons in coincidence with soft x-ray fluorescence has been demonstrated, thus enabling the elimination of line shape distortions due to post-collision interaction between the photoelectrons and core-hole induced Auger electrons. To overcome the low fluorescence yield of the first-row elements, efficient detection is needed in conjunction with a high photon flux. A new instrument combining a time-of-flight zero-kinetic-energy (ZEKE) electron spectrometer with a large photon detector near the interaction region provides a high detection efficiency. Figure 3 shows the results for N₂. The resonances below the

Figure 1 U11: Photoionization efficiency spectrum of IO ($m/s = 143$) at a nominal resolution of about 0.23 nm and 0.10 nm steps between $\lambda = 115.0$ and 130.0 nm. The arrow indicates the onset of ionization at 127.3 nm ($IE = 9.74 \pm 0.02$ eV). The superposed lines indicate autoionization which presumably correlates with a Rydberg progression (126.2 nm/ $n^* = 5.18$, 124.3 nm/ $n^* = 6.17$, 123.2 nm/ $n^* = 7.12$, 122.4 nm/ $n^* = 8.19$, 121.9 nm/ $n^* = 9.19$, where $n^* = (R/(IE - E_n))^{1/2}$ and $R = 13.60539$ eV) that converges to an excited state of the cation at 120.0 nm (10.33₂ eV). [Z. Zhang (BNL-DAS), P.S. Monks, and L.J. Steif (NASA, MD), J.F. Liebman (U. of Maryland), R.E. Huie (NIST), S.C. Kuo, and R.B. Klemm (BNL-DAS)].

Figure 2a U13UA: Auger Spectrum of CH_4 (excitation by $h\nu = 296$ eV).

Figure 2b: Resonance Auger spectrum of CH_4 following $1s \rightarrow 3s$ excitation ($h\nu = 287.04$ eV).

Figure 2c: Resonance Auger spectrum of CH_4 following $1s \rightarrow 3p$ excitation ($h\nu = 288.00$ eV). [S.Y. Chen, and D.M. Hanson (U. Stony Brook)].

1s ionization limit in the coincidence spectrum give new information about the radiative decay dynamics. Further sensitivity enhancements are planned.

Another study on beamline X1B involves the doubly excited neutral states in CO and N_2 , following the recent finding of such 2-hole-2-particle states in the high resolution absorption spectra about 4-7 eV above the C 1s and N 1s ionization thresholds. Figure 4 shows the decay spectra due to C 1s and N 1s ionization and the decay of the doubly excited states above as well as below thresholds. The below threshold excited states have been previously obscured by Rydberg excitations in the absorption spectrum. For CO and N_2 , the 2-hole-2-particle states about 4 eV above threshold have also been observed to undergo valence autoionization.

On beamline X24A, after the successful implementation of coincidence detection of photoelectrons or Auger electrons with fluorescent x-rays (reported last year), a study to understand angular correlations in the coincidence measurements has been initiated. X-ray scattering studies on OCS and atomic Ar have also been made on beamline X24A.

Double ionization of He has been of great interest as the testing ground for understanding electron correlation. Measurements on the ratio of the cross-sections for double to single ionization of He were made in the last few years on beamlines X24A, X26C and X8A. The work has now been extended to beamline U13UA, where an accurate determina-

N_2 Ionization Threshold

Figure 3 X1B: From top to bottom, the coincidence spectrum, the ZEKE electron spectrum, and the soft x-ray fluorescence yield spectrum of the N_2 molecule. The solid line in the upper panel is a tentative four-Gaussian fit with the spacing locked to 0.31 eV. [J.-E. Rubensson, J. Lüning (KFA Jülich), M. Neeb (FHI Berlin), S. Eisebitt (U. British Columbia), B. Küpper, and W. Eberhardt (KFA Jülich)].

Figure 4 X1B: Decay spectra of CO and N₂ excited around the C 1s and N 1s ionization thresholds at 296.1 eV and 409.9 eV, respectively. The decay of the doubly excited states above threshold show strong resonant features at 268 eV for CO and at 380 eV for N₂, as can be seen in (b) and (d), respectively. The spectra in (a) and (c) show resonant-enhanced structures which are attributed to the decay of additional 2h2p states immediately below threshold. The leading ripple peak structure in all spectra is due to direct photoemission of the outer valence orbitals. The valence photoemission spectra of CO and N₂ are shown at the bottom as dotted lines. [M. Neeb, A. Kivimäki, B. Kempgens, H.M. Köppe, and A.M. Bradshaw (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin)].

tion of the ratio from the double ionization threshold at 79 eV to 700 eV is the goal. The experiment utilizes time-of-flight detection of He⁺ and He⁺⁺ with Rayleigh scattering as the prompt signal. Figure 5 shows a comparison of data with theory.

Figure 5 U13UA: Comparison of present results with two early theoretical predictions. [J.C. Levin, G. Bradley Armen, and I.A. Sellin (U. Tennessee)].

SCIENCE

ENERGY DISPERSIVE DIFFRACTION

Syed B. Qadri

Naval Research Laboratory

Energy dispersive diffraction techniques at NSLS are extensively used in obtaining diffraction from samples of microscopic dimensions such as with specimens contained in diamond-anvil cells (DAC) under extreme pressure and temperature conditions. The essential components of energy-dispersive x-ray diffraction (EDXD) system consist of an Si(Li) or intrinsic Ge detector and a FET preamplifier, both cooled by liquid nitrogen, and a multichannel analyzer (MCA). The use of this system in conjunction with the X17C beamline at the NSLS, which produces polychromatic x-rays using a high magnetic field of the superconducting wiggler (4.6–4.8 Tesla), has made possible the study of solid state phase transitions and equations of state in real time. With the advancement of diamond anvil cell technology, pressures as high as 2.5–3.0 Mbar which are comparable to the pressure at the center of the earth (~3.5 Mbar) are routinely achieved. In the diamond anvil cell, the specimen is confined in the hole of a gasket between opposing diamonds and the pressure is applied by mechanically squeezing the diamonds. In the case of multi-megabar pressures, the size of the gasket hole hence the sample size is reduced to as small as 10 μm diameter. Thus the use of conventional x-ray sources becomes impractical, and intense synchrotron radiation becomes essential for high pressure research. The use of energy-dispersive x-ray diffraction is not limited to structural information at extreme pressure and temperature conditions, it is also extremely useful in single-crystal studies of microscopic dimensions approaching 40 nm diameters with volumes of attoliters. Highlights of the most recent work performed using EDXD techniques and wiggler-produced synchrotron radiation on beamline X17C are reviewed in this article.

Since iron is the main component of the earth's

Figure 1 X17C: The energy dispersive x-ray diffraction patterns of the laser heated iron at 125 GPa, showing that a new diffraction line (arrow) develops as the diffraction lines from ϵ -Fe disappear above 3000 K. The 100, 101, 110, and 112 reflections of ϵ -Fe are located at 17.33, 19.71, 30.07, and 35.81 keV, respectively ($E_d=33.94 \text{ keV \AA}$). The heating cycle starts with the bottom curve and moves upwards. (C. S. Yoo, J. Akella, A. J. Campbell, H. K. Mao, and R. J. Hemley, *Science*, **270**, 1473, 1995).

core, studies of phase transitions at high pressures and temperatures are of fundamental interest to geophysicists. C. S. Yoo from Lawrence Livermore National Laboratory in collaboration with associates at Carnegie Institution of Washington (CIW), using an integrated diamond-anvil cell, x-ray, and laser heating apparatus examined the iron phase diagram by directly probing the crystal structure of the phases *in situ* to 130 gigapascals (GPa) and 3500K. Their system consisted of three components (i) a Nd-yttrium-aluminum-garnet laser heating system to heat the sample in the diamond-anvil cell, (ii) a microscope system to measure temperature and view the sample for alignment and direct observation, and (iii) a synchrotron x-ray and energy dispersive diffraction system. Figure 1 shows the x-ray diffraction patterns of the laser heated iron at 125

Figure 2 X17C: Constraints for the phase diagram of iron. Various symbols indicate the phases of iron as determined by *in situ* x-ray diffraction at high pressures and temperatures: liquid iron (○), ϵ -Fe (●), ϵ' -Fe (△), γ -Fe (◐), and new crystalline (◑). The area indicated by the large rectangle constrains the location of the ϵ - γ liquid triple point. The hatched area indicates the P-T region of which the ϵ' phase forms between 15 and 40 GPa. Previously reported phase boundaries are also reproduced for comparison: melting lines are reproduced from R. Boehler, *Nature*, **363**, 534, (1993) (upper dashed lines), from S. K. Saxena, G. Shen, P. Lazor, *Science*, **260**, 1312, (1993); *ibid.* **264**, 405, (1994), (upper dotted line, and from Q. Williams *et al.*, *Science*, **236**, 181, 1987, (dashed-dotted line), and e-b boundaries are shown from R. Boehler, *Nature*, **363**, 534, (1993), (lower dashed line) and from S. K. Saxena *et al.*, *Science*, **260**, 1312, (1993); *ibid.* **264**, 405, (1994) (lower dotted line). (C. S. Yoo, J. Akella, A. J. Campbell, H. K. Mao, and R. J. Hemley, *Science*, **270**, 1473, 1995).

GPa and Figure 2 shows the phase diagram of iron. Iron in the hexagonal close-packed (hcp) phase (ϵ -Fe) is stable from 50 to 110 GPa at high temperatures. The wide pressure range stability of ϵ -Fe indicates that this polymorph should be the most relevant solid phase for earth's core. [see C. S. Yoo, J. Akella, A. J. Campbell, H. K. Mao, and J. R. Hemley, *Science*, **270**, 1473, (1995)].

S. K. Saxena and his colleagues from the Institute of Earth Sciences, Uppsala University in collaboration with CIW using apparatus similar to the foregoing, showed that ϵ -phase transforms to another phase (possibly a polytype double-layer hcp) at a pressure of about 38 GPa and at temperatures between 1200 and 1500K. This information has important implications for the phase relations in the earth's core. [see S. K. Saxena, L. S. Dubrovinsky, P. Haggkvist, Y. Cerenius, G. Shen, and H. K. Mao, *Science*, **269**, 1703-1704, (1995)].

Iron sulfide (FeS) has been found in many meteorites and is a possible component of the cores of Earth, Mars and other terrestrial planets. In models simulating the internal structure of the planets, accurate determinations of phase relations and densities of FeS at high pressure and high temperature are required. Previous phase transformations of FeS were performed at high pressure and at ambient temperature. Y. Fei and his colleagues from CIW using synchrotron x-ray diffraction measurements showed that FeS transforms to a hexagonal NiAs superstructure with axial ratio (c/a) close to the ideal packing ratio of 1.63 at high pressure and high temperature. They also determined the densities of FeS IV at high pressure and temperature and used these data to evaluate the depth of the Martian core-mantle boundary and the sulfur content of the core. Figure 3 shows the EDXD diffraction spectra of the different phases of FeS and Figure 4 the experimentally determined phase diagram. [see Y. Fei, C. T. Prewitt, H. K. Mao, and C. M. Bertka, *Science*, **268**, 1892-1894, (1995)].

The equation of state and phase stability are the most fundamental properties in the understanding the physics of materials at ultra high pressures. However, the reliability of equation of state determinations at large compressions is uncertain because the stress state at multimegabar static pressures is not well understood.

Duffy, Hemley and Mao from CIW using synchrotron x-ray diffraction in a diamond anvil cell determined the equation of state, elasticity and shear strength of magnesium oxide to 227 GPa. Their equation of state can describe ultrasonic, shock, and static compression for MgO. They showed that it is possible to characterize material strength and elastic anisotropy at ultra high pressure directly from diffraction data. Their results also show that there are significant changes in the degree and character of the elastic anisotropy of MgO at high pressure and that the strength at high pressures differs significantly from predictions based on low-pressure measurements. [see T. S. Duffy, R. J. Hemley, and H. K. Mao, *Phys. Rev. Lett.*, **74**, 1371, (1995)].

(Mg,Fe)SiO₃ perovskite is the predominant phase of the lower mantle and the most abundant mineral in Earth. C. Meade, H. K. Mao and J. Z. Hu from CIW

Figure 3 X17C: Energy-dispersive x-ray diffraction spectra of the high-pressure-temperature phase of FeS (FeS IV) (upper spectrum) and the high pressure phase (FeS III) (lower spectrum). The diffraction pattern of FeS IV was indexed with a hexagonal cell. The hkl indices are indicated for each diffraction peak. The peak positions for FeS III are indicated by the interplanar d spacing in Å. [Y. Fei, C. T. Prewitt, H. K. Mao, and C. M. Bertka, *Science*, 268,1892, (1995)].

studied the crystallography of Earth's lower mantle using synchrotron x-ray diffraction from a laser-heated diamond anvil cell. Their experiments show that silicate perovskite maintains its orthorhombic symmetry at 38 GPa and 1850K. Their measurements at 65 and 70 GPa provide evidence for a temperature-induced orthorhombic-to-cubic phase transition and dissociation to an assemblage of perovskite and mixed oxides. If these phase transitions occur in Earth, they will require a significant change in mineralogical models of the lower mantle. [see C. Meade, H. K. Mao, and J. Z. Hu, *Science*, 268, 1743, 1995].

Some of the other highlights of the work from CIW include the work of Duffy *et al.* on the single-crystal of brucite, $\text{Mg}(\text{OH})_2$, to 14 GPa in a quasi-hydrostatic pressure medium using a DAC and EDXD synchrotron x-ray diffraction [see T. S. Duffy, J. Shu, H. K. Mao, and J. R. Hemley, *Phys. Chem. Minerals*, 22, 277, 1995]. They proposed the structural change in brucite is driven by a destabilization of the H substructure as the materials are compressed. No evidence was found for a transition involving the Mg-O substructure over the pressure range of the experiments.

Skelton and associates from the Naval Research Laboratory (NRL) have studied a number of high temperature superconductors, in search of evidence of structural inhomogeneities. By illuminating the samples with 10 μm beam, small changes in the c-axis lattice were detected and were interpreted as evidence of variations in the oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$. For all samples, the data reveal small structural variations on a spatial scale 10 to 20 μm , heretofore not seen. For the $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ the observed effect is believed to be due to changes in oxygen. In the case of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$, the observed structural variances are interpreted in terms of changes in the Ce content. These results emphasize the need for caution in interpreting experimental results for high temperature superconductors (HTS). As the smaller beam sizes are achieved, they are likely to observe significant structural defects in sub- μm length scales. Ideally, as spatial resolution increases, more subtle questions regarding the nature of the defect structures and their origins can be answered [see Skelton *et al.*, *SPIE*, 2516,160,1995].

Figure 4 X17C: Experimentally determined phase diagram of FeS. Experimental data (reported only near the phase boundary) are represented by symbols. (m) FeS I, NiAs-type structure with a $(\sqrt{3}a, 2c)$ unit cell; (1) FeS II, MnP-type structure; (o) FeS III, monoclinic?; (e) FeS IV, NiAs-type structure with a $(2a, c)$ unit cell. [Y. Fei, C. T. Prewitt, H. K. Mao, and C. M. Bertka, *Science*, 268,1892, (1995)].

Figure 5 X17C: EDXD spectra of 8.2 nm particle size PbS taken at different pressures. The onset of cubic-to-orthorhombic transition at a pressure of 30.0 kbar can be realized.

G.S. Cargill III and P.C. Wang from Columbia University in collaboration with IBM Research and BNL Applied Science are developing a system for measuring strain, microstructure and composition using EDXD with micron or submicron spatial resolution on beamline X26C. They use 5 to 30 keV photons collimated and concentrated by a tapered glass capillary. [See their abstract under X26C abstracts]. In their experimental setup the Laue patterns are measured using an area CCD detector while the lattice spacings and compositions are measured using an energy sensitive Si detector.

The Pd-H system is probably the most extensively investigated of all metal-hydrogen systems. Nevertheless, some of its properties at high hydrogen concentration still remain unexplained. Skelton *et al.* from NRL using up to 80 keV x-ray photons monitored the crystallography of a microspot $18 \times 10^{-12} \text{ m}^3$ in volume, as D was electrochemically loaded into a 1 mm diameter Pd wire. Because of the penetrating power of the high energy x-ray photons available on X17C, this spot could be located anywhere within wire. Using this, the α - β transition induced in the Pd by the absorption (or desorption) of D was monitored from the outer edge to the core of the wire. Results show that, although the α -phase forms rapidly at both the surface and core, there is considerable delay in the initiation of the β -phase at the core compared to that at the surface.

Qadri *et al.* from NRL initiated the work to determine the effect of nanometer size particles on the pressure induced phase transitions. For this the PbS particles were synthesized by a new technique. The three-dimensionally periodic and interconnected mesomorphous structure of a bicontinuous cubic phase was controlled through the pore size and ionic diffusion. The particles were extracted from the lipid micro structure and capped with thiol molecules. Their size and crystallinity were characterized by TEM and XRD. The high pressure studies were performed using polychromatic x-rays on X17C at NSLS. At 2.5 GPa pressure and room temperature, PbS transforms from the NaCl-structure to an orthorhombic phase. This transition is sluggish and accompanied by a large hysteresis. The results show a significant increase in the on-set of the transition pressure as the particle size was reduced. Figure 5 shows a series of EDXD spectra of PbS samples of 8.2 nm particle size as a function of increasing pressure.

SCIENCE

LITHOGRAPHY, MICROSCOPY, AND TOMOGRAPHY

G. P. Williams
NSLS

X-RAY MICROSCOPY

General

The X1A x-ray microscope beamline serves an increasing number of users, to the point where beam time is oversubscribed. Activities which have been reported on in previous years continue to see further development. In the coming year, the beamline will be upgraded to have two, independently controlled monochromators with an optimized design providing increased flux and monochromaticity. This will lead to a downtime of several months, but increased productivity afterwards.

The Stony Brook group continues to carry out studies involving imaging and chemical state mapping in biological samples. Also, at Stony Brook, a new scanning x-ray microscope system is being developed by J. Maser *et al.* in which the specimen will be held at liquid nitrogen temperature in a vacuum chamber. This will allow the examination of biological specimens which have been frozen with water in an amorphous (rather than crystalline) state, leading to more faithful specimen preparation and improved radiation robustness. Commissioning of the system began at the end of the year, and first cryo experiments are expected in the coming year.

The North Carolina State group has continued studying various polymer samples in collaboration with Dow Chemical, AlliedSignal and DuPont. X-ray Absorption Near Edge Structure, or XANES, microscopy is ideally suited for the study of multicomponent polymers and their morphology, structured and layered polymer systems, as well as the microchemical characterization of precipitates of unknown chemical composition. Soft X-ray Transmission microscopy operated in the XANES mode is also an excellent tool for acquiring high quality spectra from a variety of polymers which would be difficult to accomplish otherwise due to problems with sample preparation. Linear Dichroism microscopy has been utilized to semi-quantitatively determine the lateral order of Kevlar fibers.

New Zone Plates

In collaboration with Don Tennant of AT&T Bell Laboratories, Steve Spector and Chris Jacobsen of Stony Brook have recently made new zone plates for the scanning transmission x-ray microscope which have an outer zone width of 30 nm as opposed to the previously available 45 nm (the resolution scales with zone width). These zone plates were fabricated using a new electron beam lithography system at Bell Labs, and were patterned by etching germanium. Present efforts are aimed at boosting the efficiency up to the level predicted by theory, and at using nickel plating for zone plate fabrication.

Dark-field Imaging

The Scanning Transmission X-ray Microscope (STXM), located at beamline X1A, usually forms absorption images of biological specimens using Fresnel zone plates. The wavelength is tuned to where there is a large difference in the x-ray absorption of carbon and oxygen to image micron-thick cells in water, for example. Signals other than absorption can be used to form an image, such as in dark-field imaging where only the x-rays scattered by the specimen are detected. Studies by Henry Chapman, Chris Jacobsen, and Jenny Fu (all of the department of Physics, SUNY at Stony Brook) have shown that dark-field imaging is a particularly sensitive way of imaging colloidal-gold labels in cells. These small (on the order of 20 nm in diameter) particles can be bound to specific antigens, genetic sequences, cellular organelles, or proteins so that specific functions of a cell can be localized. The techniques are highly developed in the electron microscopy community for labelling thin sections of cells, but whole cells are too thick to be imaged by electrons. Dark-field x-ray microscopy forms the bridge between fluorescence confocal microscopy and electron microscopy.

Even though the label particles are smaller than the resolution of the microscope they are still easily detected in the dark-field mode. A whole human fibroblast cell is shown in Figure 1 which has had the protein tubulin labelled with colloidal gold. The image is actually a

composite of a bright-field image and a dark-field image. The bright-field signal is shown in grey-the color indicates the x-ray absorption, mainly due to carbon. The dark-field signal is shown in red, and reveals only microtubules (fibers composed of tubulin). The same cell was also examined in an electron microscope. While the resolution was much better, the electron microscope could not show the microtubules in regions of high carbon density, such as across the nucleus. The cell was prepared and labelled by Karen Hedberg, University of Oregon.

Phase Retrieval Experiments

Phase retrieval of images collected in the STXM at beamline X1A has been achieved by applying the new method of Wigner-distribution deconvolution. This research, by Henry Chapman of SUNY at Stony Brook, has yielded very accurate high-resolution images of the phase and amplitude of the x-ray transmission of various specimens, such as the 0.5-micrometer-diameter latex sphere shown in the Figure 2.

To determine the x-ray phase retardation of an object, microdiffraction patterns (or coherent convergent-beam diffraction patterns) are collected in the STXM with a CCD detector. As the specimen is scanned in two dimensions, a 2-D microdiffraction pattern is collected at each point in the scan. The map of intensity recorded in a single element of the CCD versus the specimen position is a coherent image that can be thought of as being formed by a self-interferometric process. By four-dimensional Fourier transformation, the ensemble of images is analysed to find the relative phases of all pairs of image points that are separated by particular displacement vectors, from which a phase map can be determined. This method has also been used to map the phase errors (aberrations) of an Fresnel zone plate at the x-ray wavelength at which it is used for forming images, and for measuring the mutual coherence of an x-ray beam. In addition, super-resolved STXM images could be acquired by this method in making use of the high-angle diffraction data.

Figure 1 X1A: Composite of dark-field and bright-field image of whole human fibroblast cell. Measurements made by Chapman *et al.*

IR MICROSCOPY

General

At the U2B beamline there have been a number of studies using the IR microspectrometer which is a Spetra-Tech IRuS instrument operated by Northrop-Grumman Corporation and the NSLS. This instrument operates at a spatial resolution close to the diffraction limit, i.e in the 3-15 micron range. It has been used for studies of materials ranging from semiconductors (Larry Carr, Northrop-Grumman) to human hair (Dave Wetzel *et al.*, Kansas State U.) to minerals (Nicole Guilhaumou, Laboratoire de Geologie URA 1316, Paris, France and Paul Dumas LURE-CNRS, Centre Universitaire, Paris-Sud).

Semiconductors and Devices

Larry Carr of Northrop-Grumman has studied the ternary II-VI semiconductor compound CdZnTe, which is used for both electronic and optical applications.

Figure 2 X1A: (a) An image of the phase retardation of 400 eV x-rays transmitted through a 0.5-micrometer-diameter latex sphere, and a plot (b) from that image compared with the calculated phase. In (c) is part of the data set of coherent images collected in the STXM used for retrieving the phase. The location of each image in the grid is indicative of the location of the CCD pixel from which that image was formed. The nine images with bright backgrounds, for example, were recorded by CCD pixels that are illuminated by the annular pupil of the zone-plate. Each image is 1.5 micrometer wide. Measurements made by Chapman *et al.*

The studies are of the material in wafer form. Precipitates of Te were found in the material. These precipitates are only about 10 microns in diameter and thus beyond the capability of conventional IR microspectroscopy. 2-D maps can be made using the difference in transmission of Te in the IR as a contrast mechanism. In another study, Larry Carr also studied epi-layers for opto-electronic devices, and particularly those called vertical cavity surface emitting lasers. These are complex patterns of layers of III-V semiconductor compounds grown epitaxially on GaAs. These particular devices will see applications as flat panel displays.

Human Hair

Dave Wetzel (Kansas State University), in conjunction with Kathryn Kalasinsky (Div. of Forensic Toxicology, Armed Forces Inst. of Pathology, Washington, DC), has been studying drugs of abuse and their metabolites, deposited in human hair. The spatial resolution of a few microns permits drug traces to be mapped within thin longitudinal hair sections. Furthermore 5 microns corresponds to about 20 minutes of hair growth, so that the timing of drug use might be able to be determined. These studies are difficult since the absorption strength of the carbonyl band for example, a product of cocaine use, is only a few tenths of a percent. However the brightness and stability of the source do permit these measurements to be made.

Fluid Inclusions in Rocks

Nicole Guilhaumou (Laboratoire de Geologie URA 1316, Paris, France) and Paul Dumas (LURE-CNRS, Centre Universitaire, Paris-Sud) have studied fluid inclusions in oil-bearing mineral samples. These inclusions are in fluorite and were indeed found to contain oil, and CO₂ as bubbles. Measurements of the integrated intensities for the respective vibrational modes, allow chemical maps to be obtained for each component within the fluid inclusion. In Figure 3 (See Section Divider on Page 88) we show a photograph of an inclusion and then maps for the oil and the CO₂ (namely the antisymmetric stretch mode of CH₂ at 2920 cm⁻¹ and the symmetric stretch mode of CO₂ at 2335 cm⁻¹). One clearly sees the location of these two components inside the inclusion. The relative intensity is related to the local density. If the oil is homogeneous, the various intensities are related to the thicknesses of the areas probed. In addition, the frequencies of the modes change with pressure, opening up the possibility of determining the pressure-temperature situation when the inclusions were formed. One can also test for water and in this case, no water bands were detected inside the inclusion.

Towards Near-Field IR Microspectroscopy

At the present time, the spatial resolution achieved at the IR microspectroscopy facility at beamline U2B is limited by diffraction to the wavelengths in use, i.e from 3 - 15 microns. Near-field microscopy is a method for extending this spatial resolution by confining the light to a structure smaller than the wavelength, typically through the use of tapered light guides. However, such structures are often highly inefficient and appropriate only for very high brightness sources such as lasers. In a study using a 13 micron pinhole to confine the beam, Larry Carr found that it was possible to drive waveguide modes in the

pinhole structure, resulting in an enhanced throughput for particular wavelengths. This is illustrated in Figure 4a, which shows the transmitted intensity pattern as a function of illumination position across the pinhole. Each panel represents an intensity "map" for a particular wavelength. At the top left is the case where the wavelength is short compared to the pinhole, so normal geometric optics describe the situation. At top right, the wavelength is 7 microns and two regions of enhanced throughput are observed. The pattern suggests that an 01 mode is being excited within the pinhole structure. Similarly, a single central region of enhanced throughput is observed for wavelengths near 14 microns, indicating that the 00 mode is excited. Coupling to such modes is one method for improving the throughput while confining the light to a size substantially smaller than its wavelength. An understanding of the transmission properties of this and similar structures should be useful in optimizing an efficient near-field tip structure for microspectroscopy with synchrotron radiation. Extending this concept to smaller dimensions, in Figure 4b we show the ratio of 2 transmission spectra through a 3 micron pinhole, which in the absence of noise would give a straight line at 1. It can be seen that good performance is obtained even for wavelengths to almost 3 times the pinhole size. The actual spectrum is shown in the inset.

Microtomography

A computed microtomography users' facility is presently being developed at X27C with the support of BNL's Computing and Communications Division (CCD), Mobil Corporation, and GTE. The facility will provide non-destructive volumetric images of specimens of variable size with resolutions from 1 to 100 microns, depending on the instantaneous field of view. The facility presently includes a 12-bit digital ccd camera to capture 2-D radiographs of each view angle. These radiographs are then processed within a reconstruction program to create 2-D slices. The slices can be stacked to create a volume rendering using graphics programs such as Data Explorer, Iris Explorer or IDL. A user facility under development at CCD will also allow stereoscopic viewing of the reconstructed volumes in the near future.

Figure 4a U2B: (a). Towards near-field IR microspectroscopy. Intensities measured through a 13 micron pinhole at various wavelengths by Larry Carr, (Northrop-Grumman).

Over the past year, 2-D slices as well as volume renderings have been obtained for pore structures of several seal rock and oil reservoir core samples provided by Mobil Corporation. The pore structure of the samples were resolved to 3 microns. Other samples analyzed at this CMT facility at X27C include meteorites, lead sulfate crystals growing in a glass matrix, and synthetic rock. Figure 5 (See Cover) shows a volume rendering of a test sample of 100 micron diameter glass spheres in a capillary of 5 micron wall thickness.

X-RAY FLUORESCENCE MICROPROBE

The X26A x-ray fluorescence microprobe can map trace elemental distributions of ppm concentrations at a spatial resolution of about ten micrometers and has been used by Saša Bajt, Steve Sutton (CARS, U. of Chicago), Patterson Nuessle (SREL, U. of Georgia) and collaborators for a variety of systems from biology to geology. Increasingly, the microprobe is also being used for x-ray

Figure 4b U2B: Reproducibility (noise) as a function of wavelength through a 3 micron pinhole showing the increased performance at shorter wavelengths due to the wave-guiding, near-field effects discussed in the text. The actual spectrum is shown in the inset.

absorption spectroscopy measurements when both good spatial resolution and the sensitivity are required. Scientists from the Earth, planetary, and environmental sciences are still the major users of the beamline, although we observed increased interest among scientists from agronomy and forestry departments.

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scans show is that, unlike major elements, trace elements such as Y display oscillatory zoning which varies by orders of magnitude in abundance (3 to 4000 ppm). These variations in trace element zoning correspond with changes in textural zoning within the garnet defined by the abundance of inclusions, something the major element zoning does not do. Thus, both textural and trace element zoning profiles suggest that these garnets grew from discontinuous reactions.

Trace element zoning was studied also in alpha and beta quartz to understand their significance for the origin of comb layering in porphyry inclusions (US Geological Survey). A continued study on determination of trace element composition of stratospheric interplanetary dust particles (large versus small) and observation of Br loss in these particles as a function of time for which particles were exposed to the synchrotron radiation was performed (SUNY at Plattsburgh and CARS).

In addition to a solid state detector, fluorescence has also been detected with a wavelength dispersive spectrometer (WDS). This has enabled a study of intracrystalline

One of the interesting experiments using trace element analysis and mapping was performed on garnets by SUNY at Stony Brook (For Figure 6 See Section Divider on Page 64). Major element compositional zoning in garnets (of the elements Fe, Mn, Mg, and Ca, for example) is commonly used to evaluate the pressure, temperature, and reaction history of metamorphic rocks. The garnets in this rock display smooth increases in Fe abundance (30 to 38 wt. % FeO) and decreases in Mn abundance (5 to 0.4 wt. % MnO) from the core to the rim. Such zoning profiles are common in garnets and are typically interpreted as the product of a single garnet-forming reaction during a single episode of metamorphism with increasing pressure and temperature. However, what the synchrotron x-ray fluorescence (SXRF)

rare earth element (REE) distributions in fluoroapatite. Observed partitioning of REEs argues against differential incorporation due to growth rate anisotropies but it supports the proposed model that differences in the atomic structure between $\langle 001 \rangle$ and $\langle 011 \rangle$ steps leads to differential incorporation in apatite (SUNY at Stony Brook). A reversal in the REE partitioning trend was observed for Pr and Nd suggesting that ion size has an effect on the partitioning between nonequivalent steps. Another study focused on the three dimensional spatial resolution of compositionally distinct growth sectors and subsectors in mineral crystals. These sectors and subsectors preserved a record of surface processes and growth mechanisms. The goal of this study at the moment is to explain topaz crystal growth on a molecular scale (SUNY at Stony Brook).

The determination of ferric/ferrous ratios in micrometer regions on amphiboles and glasses using the energy position of the pre-edge peak in Fe XANES spectra showed a good agreement with the results obtained by Mossbauer spectroscopy and wet chemistry techniques. This confirms previous results that the position of a pre-edge peak in the absorption spectrum is not very sensitive to the coordination geometry when using appropriate standards (Rutgers U. and CARS). Another way of looking at the near-edge region is studying pre-edge inelastic scattering using a WDS (BNL and CARS). Further progress has been made on determination of the structure and speciation of zinc complexes in individual fluid inclusions (only about 50 microns in size) using micro-EXAFS. Experiments at elevated temperatures, up to 350 degrees Celsius, were done with a well calibrated heating stage. The results suggest that Zn complex remained predominately ZnCl_4^{2-} , the dominant complex of Zn observed at room temperature, but further experiments at even higher temperatures are underway (South West Missouri State U., St. Francis Xavier U. and CARS).

Environmental studies included determination of oxidation states of Cr contaminated solid particles and the efficiency of in situ Cr reduction methods. Cr(VI)/Cr(III) ratios could be probed on particles as small as 40 microns and near-edge structure was correlated to EXAFS measurements (SREL). The effect of oxidation state on chromium leaching for a contaminated/stabilized soil was also studied by a group from the US Army Corps of Engineers and scientists from Purdue University. The Savannah River Ecology Institute group conducted time resolved in situ Fe XANES measurements on clay minerals which catalyze the oxidation of organo-boron complexes used in reclamation of radio-Cs contaminated nuclear waste. Another type of time resolved *in situ* experiment was carried out to track selenium and chromium transport

and reduction across the boundary between ponded waters and sediments (LBL). The results showed reduction of Se(VI) to Se(IV) and ultimately Se(0) within specific zones in the sediments and were consistent with diffusion-limited transport calculation. Micro-XANES ruled out the possible formation of colloidal Se(0) and organo-Se compounds in these ponded waters. The chromium oxidation state was studied in a CCA pressure treated wood and it has been found that Cr was reduced to pure Cr^{3+} , on the surface and in the inner part of the wood (Forestry Dept., U. of Wisconsin). Iodine XANES measurements were acquired in a He environment to study iodine sorption on different minerals. Intriguing results showed that magnetite, biotite and pyrite (Fe rich minerals in this study) underwent different reactions when in touch with iodide or iodate solutions as compared to Fe poor minerals (BNL).

In addition, a new 13 element Ge detector was successfully used to collect data with a 10 micron monochromatic collimated beam to study olivine grains from chondrites (primitive meteorites that usually contain mm sized spheres called chondrules) that are usually only 20-50 microns in size and have very low concentrations of Cr (U. of New Mexico and CARS). Without the 13 element Ge detector this experiment would be impossible. The results obtained are significant because, based on the fact that transition of Cr^{2+} to Cr^{3+} occurs over a very narrow range of oxygen fugacity, the micro-XANES approach may lead to highly sensitive method for determining the redox conditions of formation for individual chondrules.

Plant and Wood Disease;

The blast disease of rice, caused by the fungus *Pyricularia grisea*, is one of the most important plant diseases worldwide because rice is a major source of food for 60% of the Earth's population. Manganese is an essential mineral element for photosynthesis, lignin synthesis, and other plant metabolic functions in its Mn^{2+} or Mn^{3+} forms, but when oxidized to Mn^{4+} it precipitates as physiologically unavailable Mn oxides and hydroxides. In the healthy areas of the leaf all of the Mn is in the physiologically available Mn^{2+} form. In the blue area, which corresponds to the lesion in the photograph Figure 7, 80% of the Mn is present as Mn^{4+} (See Section Divider on page 96). Thus most of the Mn in the lesion is in the unavailable Mn^{4+} form. Oxidation of soluble Mn^{2+} to give insoluble Mn^{4+} oxides may be the first step in the mechanism by which the fungus infects healthy plants. If so, this research may provide important new information for combating this devastating plant disease.

Manganese near-edge spectroscopy was also used to study the effects of two different fungi on wood (Forestry Dept., U. of Wisconsin). One study was an *in vivo* measurement of the Mn oxidation states on wood that had been attacked by a tree disease fungus. The other was to study a very dangerous white-root fungus (wood decay fungus). The results suggest that these quite different fungi both contain enzymes that oxidize Mn^{2+} to Mn^{4+} .

Electrochemistry

The x-ray fluorescence microprobe was used to study the corrosion resistance of stainless steels. Presence of molybdenum in stainless steels is believed to improve the corrosion resistance, and different models have been proposed on how and why this happens. Some models suggest that molybdenum forms a salt layer during the dissolution of the steel, and this process was studied *in situ* at X26A. Scanning the beam across the steel, a salt layer on the steel, and the concentrated dissolution products within an artificial pit, concentrations changes of the constituent alloying elements were monitored. Results suggest that the salt layer was mainly formed by iron chloride and not molybdenum therefore negating proposed corrosion inhibition by a molybdenum forming salt layer (BNL).

On the X26C beam line an experiment was performed using x-ray fluorescence with high energy resolution spectrometer (total energy resolution of 1 eV or better). The analysis of x-ray fluorescence with this high energy resolution can provide detailed information on the electronic structure of the sample in addition to quantitative elemental analysis of the sample. Preliminary results from a series of chromium oxides demonstrate the sensitivity of this technique to the oxidation state of the sample (NSLS and CARS).

LITHOGRAPHY

Extreme Ultra-Violet Projection Lithography

AT&T Bell Labs continues to progress on beam line U13UB with the development of Extreme Ultraviolet Lithography (EUVL). The technique is the diffraction limited imaging of circuit features with dimensions around 100nm using multilayer coated mirrors and light of wavelength around 13nm. The technique is one of the main contenders for the new lithography technology that is scheduled to be required around the turn of the century. The AT&T EUVL program at Brookhaven is part of a larger coordinated effort involving Intel, AMD, Sandia National Laboratory, Lawrence Livermore National Laboratory, Lawrence Berkeley National Laboratory, and

Sematech. This year Kiyosho Fujii of NEC, who has been working on EUVL for over a year, joined the AT&T group.

The main progress this last year has been the assembly and commissioning of a new EUVL printing camera capable of imaging over a large field (For Figure 8, See Section Divider on Page 73). Significant progress has also been made on the interferometry techniques that are required to be developed in this wavelength range. The 13nm interferometer based on U13UB has demonstrated that lateral shearing phase measuring interferometry can measure the wavefront of 13nm light to 0.02 waves rms. This is the required accuracy for measuring the wavefront at the image plane of EUVL cameras and represents one of the important first steps in the establishment of EUV interferometry.

LIGA

In recent years the technique of LIGA, a German acronym which translates to X-Ray Lithography, Electroplating, and Plastic Molding, has emerged as the cutting edge technology in the manufacture of small, high-precision mechanical devices.

At the NSLS, the X-Ray Ring provides a unique opportunity for the utilization of hard x-rays to extend high precision manufacturing using lithographic techniques to length scales on the order of centimeters. Conventional LIGA techniques typically yield structures less than 500 μ m thick. The deep penetration of hard X-rays in the resist provides the additional opportunity to fabricate true 3-D objects with re-entrant geometries, in contrast to the 2-D structures typical of standard LIGA techniques.

A research program based on this technique is currently being developed at the NSLS R&D beamline X27B by E. Johnson, P. Siddons, and C. Milne. Current activities are focused on resist exposure and processing parameters with a view to optimizing device quality.

SCIENCE

NUCLEAR PHYSICS

Craig E. Thorn
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Since beginning operations in 1990, the Laser Electron Gamma Source facility (LEGS) has routinely produced tagged-photons up to 330 MeV by backscattering laser light from 2.58 GeV electrons circulating in a storage ring of the National Synchrotron Light Source at BNL. Work is underway that will increase the energy to 470 MeV. The chief distinguishing characteristics of LEGS are the very high degree of polarization ($\sim 90\%$) of its photon beams, accompanied by very low backgrounds. The LEGS facility was constructed by its BNL staff, assisted by a group from Frascati National Laboratory, Italy. The small BNL contingent shoulders most of the burden of the maintenance and operation of LEGS, as well as organizing the development of the new instrumentation needed to maintain state-of-the-art capabilities.

Carrying out a research program requires a much larger group and collaborations with other institutions are essential. The "LEGS Collaboration" consists of BNL, Frascati, and five Universities: Rome-II, Virginia, Virginia Polytechnic Institute, South Carolina, and Ohio. This LEGS Collaboration has been responsible for $\sim 2/3$ of the scientific research. The remaining $1/3$ has been conducted by enlarged collaborations, including LEGS, with "outside" spokespersons of proposals that undergo a review process. (A basic requirement for approval of LEGS experiments is that polarization observables make a significant impact on the physics questions being addressed. This has resulted in a strong coupling to theoretical models and a focus on light nuclei.)

POLARIZED COMPTON SCATTERING FROM THE PROTON

New precision measurements of cross sections and polarization asymmetries in Compton Scattering of polarized photons from protons at 90° c.m. are presented for incident energies between 213 and 333 MeV. A long standing problem with earlier experiments that appeared to violate unitarity at the peak of the Δ is resolved. These

data have been compared to theories based on baryon resonance structure and to dispersion relations. Recent calculations using the proton polarizabilities are closest to the data, although inconsistencies are observed near the Δ resonance.

Elastic (Compton) scattering of intermediate energy photons from the proton is a potentially rich source of structure information. It is sensitive to the proton's electric and magnetic polarizabilities, to the deformation of the nucleon through the electric $\gamma N \Delta$ coupling, and even to the sign of the π^0 decay constant, F_π . There are many published calculations for Compton scattering. These can be grouped into two general categories, those based on the baryon resonance spectrum or its underlying quark structure, and those relying upon unitarity and dispersion relations to phenomenologically describe elastic scattering in terms of photo-pion production. These calculations give significantly different predictions, particularly in the region of the Δ resonance.

A lower unitarity bound on the Compton cross sections, which avoids the uncertainties of dispersion calculations, can be constructed by using π -production to evaluate the imaginary parts of the amplitudes while setting their real parts to zero. Beyond this, minimal real parts can be formed from the s- and u-channel Born and t-channel π^0 -pole graphs. These exercises lead to a common conclusion. Previously published data near the peak of the Δ resonance, and particularly at 90° center of mass (c.m.), appear to completely exhaust these bounds, if not violate them, and leave no room for the t-channel dispersive contributions.

The chief experimental background to Compton scattering comes from the $\gamma(p, \pi^0)p$ channel, where one high energy photon from π^0 -decay is detected. The cross section for this process is ~ 200 times that expected from Compton scattering. Both the $p(\gamma, \gamma)p$ and the $p(\gamma, \pi^0)p$ reactions are completely specified by two kinematic observables. In this measurement, six quantities were measured: the beam energy, the scattered γ -ray energy, the polar and azimuthal angles of the recoil proton, and the proton's TOF and energy. This large degree of kinematic

over-determination has two important consequences. First, it guarantees an accurate separation of the two competing channels, even at high beam energies. Secondly, it enables all detector efficiencies to be evaluated directly from the data itself, without resorting to simulations and thus avoiding their associated uncertainties.

The spin-averaged Compton cross sections for 90° c.m. from the present work (LEGS Exp. L8), corrected for finite detector acceptances, are plotted as the solid circles in Figure 1 together with previous results. There have been two other recent measurements of the Compton cross sections. At the Saskatchewan Accelerator Lab (SAL), simulations were used to extract the component from scattered bremsstrahlung (open circles), while in measurements with tagged photons at Mainz (cross in Figure 1), highly collimated detectors were used to isolate coincidences. Both are consistent with our results. Data from the earlier Cornell/61, Tokyo/64, Illinois/67, and Bonn/76 experiments at energies higher or lower than the Δ peak are either consistent or slightly lower than the new group of measurements from LEGS, Mainz and SAL. Why these earlier results are so dramatically lower near the resonance energy is not known.

The solid curve in Figure 1 is a prediction using the model of L'vov, in which recent (γ, p) multipoles have been used to calculate the imaginary parts of the scattering amplitudes while low energy measurements of the proton polarizabilities have been used to fix the dispersion integrals. This gives a reasonable description of the new data, except for an over-prediction near the Δ peak. The dotted curve restricts the real parts to their Born and π^0 -pole values, and the dashed curve gives the unitarity bound obtained by setting the real parts to zero. Although slightly lower bounds have been obtained with other pion multipoles, all are significantly higher near the Δ peak than the four points from Cornell/61, Tokyo/64, Illinois/67 and Bonn/76. Although these four measurements appear to be in quite good agreement, we assert that they are, nonetheless, quite wrong.

Figure 1: Spin-averaged Compton cross sections for 90° c.m. (see text for full description).

NEW MEASUREMENTS OF $D(\gamma, p)n$ AND SPIN PROBLEMS IN COUPLED $N\Delta/NN$ INTERACTIONS

New precision measurements of the reaction $D(\gamma, p)n$ taken with tagged, polarized photons, and covering a wide angular range, are presented for incident energies between 113 and 315 MeV. In the region of the Δ resonance, the photodisintegration observables can potentially be used to probe the $N\Delta$ interaction. Coupled-channel calculations are in agreement with cross sections measured with linear polarization parallel to the reaction plane but fail to account for data taken with perpendicular kinematics.

Although the Δ isobar dominates nuclear reactions from pion threshold to about 1 GeV, its interaction with the nucleon is still poorly known. Microscopic reaction models necessarily require a consistent treatment of the $N\Delta$ and NN interactions. While the parameters of the NN force can be directly determined from nucleon scattering data, the $N\Delta$ interaction must be inferred from processes such as $\pi D \rightarrow \pi NN$ and $\pi D \rightarrow NN$ for which the

Figure 2: Angular distributions at 300 MeV for the two orthogonal spin state of the $D(\gamma,p)n$ reaction (see text for full description).

Δ plays a prominent role in the intermediate state. Because of the strong coupling of the Δ to πN , realistic models must satisfy three-body unitarity, connecting reactions starting from NN , $\pi\Delta$ or $\gamma\Delta$ entrance channels, and leading to NN , $\pi\Delta$ or pNN final states. Several such calculations have been developed in recent years. In these works, the $\pi D \rightarrow \pi D$ and $\pi D \rightarrow \pi NN$ cross sections are reasonably well described, primarily because quasi-free scattering dominates there. However, pion and photon absorption channels have proven to be more challenging.

The predicted effects of the $N\Delta$ interaction are of course largest near the energy of the Δ resonance, and polarization observables are expected to be rather sensitive to the $N\Delta$ potential. The reaction $D(\gamma,p)n$ can provide an interesting test for $NN/N\Delta$ coupled-channel models since,

as first noted by Leidemann and Arenhövel, both the cross section and the beam-polarization asymmetry are sensitive to the $N\Delta$ force. Unfortunately, comparisons with existing data have tended to be somewhat inconclusive due to a rather large spread in published results. Correlating the comparisons with cross sections and asymmetries, which might help remove some of the ambiguities, has been problematic because the two have never been measured in the same experiment. We present here highlights of recent measurements of the $D(\gamma,p)n$ reaction at the LEGS facility, which are the first to directly measure $\sigma_{\parallel}$ and $\sigma_{\perp}$. Angular distributions at 300 MeV for the two orthogonal spin-states are shown in Figure 2.

In the $\gamma+N$ system, delta excitation is almost purely $M1$, although when transformed to the deuteron-CM many magnetic as well as electric multipoles contribute. The dotted curves in the figures have been calculated by decomposing the elementary M_{1+} (isospin-3/2) multipole of $\gamma+N$ into a sum of Born and resonant terms. The resonance part was parameterized with a Breit-Wigner shape and the $\gamma N\Delta$ coupling was extracted from the fit to the M_{1+} (3/2) amplitude, as determined from $N(\gamma,p)$ data. In the $\gamma+\Delta$ CM frame, all multipoles with $L \leq 4$ were included. In this fitting procedure, the $\gamma N\Delta$ coupling was allowed to be both complex and energy-dependent, thereby absorbing the effects of pion-rescattering, while

preserving unitarity. The result reproduces the general features of the cross sections and polarization observables, particularly the shift of the resonance position from the free $N\Delta$ value (317 MeV) which is due mainly to pion-rescattering, and the negative asymmetry in the region of the resonance which reflects the spin dependence of the elementary $\gamma+N$ amplitudes. Nonetheless, the dotted curves significantly underestimate the data in the region of the delta resonance.

The discrepancy between these predictions and the data increases with energy, suggesting that the method of decomposing the amplitudes into background and resonant components is incomplete. Greater flexibility in the models can be obtained by dropping the Born terms in the $\gamma+N$ amplitudes and refitting a modified $\gamma N\Delta$ coupling of

the elementary $M_{1+}(3/2)$ multipole, now purely resonant, to $N(\gamma, p)$ data. Such a procedure has the potential for double-counting pion-exchange current (π -MEC) contributions. This effect has been estimated and the associated uncertainty is shown as the light-shaded band. Since the amplitudes certainly must contain non-resonant terms, the improvement obtained with this effective coupling suggests that the use of static π -MEC is inadequate and non-local effects are important.

In the region of the Δ resonance, the band of curves corresponding to the modified $\gamma N \Delta$ coupling are centered slightly above the total cross section data, while their predictions at 90° are consistently low. This is due to a depression in the calculated angular distributions near 90° , which grows with energy. A similar "90°-dip" is a common feature of most $\gamma \Delta \rightarrow p n$ calculations near 300 MeV, even appearing in earlier works that did not include coupled-channel treatments.

The behavior of the cross section measured with parallel kinematics (Figure 2, bottom), is quite well reproduced by the calculation with the modified $\gamma N \Delta$ coupling, and even the fitted- $\gamma N \Delta$ curve has the correct shape. The apparent "90°-dip" arises entirely from the

predictions for the perpendicular spin orientation (Figure 2, top). Although interference with the Born amplitudes, which contain high angular momentum components, can potentially affect angular distributions, this is evidently not the origin of the 90° depression since the fitted- $\gamma N \Delta$ calculation, which explicitly includes the Born terms, has a similar shape. In addition, the modified- $\gamma N \Delta$ predictions for are consistently higher than the data at forward and backward angles, although both the calculations and the data for converge to the values at 0° and 180° where the azimuthal polarization angle becomes undefined.

At present, there is no clear explanation for the success of the coupled-channel calculations in one polarization kinematics and their failure for the orthogonal state. Spin observables provide a considerably more sensitive test of the angular momentum modeling than cross sections. Although the model parameters of the calculations discussed here were fitted to NN phase shifts, all assumed static NN potentials, with retardation effects included only in the $N \Delta$ and $NN-N \Delta$ -transition potentials. The additional use of retarded potentials in the NN interaction could significantly alter the angular momentum decomposition.

Figure 3: SPHICE, a Strongly Polarized Hydrogen and Deuterium ICE Target, and SASY, the Spin ASYmmetry Array, at LEGS.

In summary, precise values for the cross section and beam polarization observables in deuteron photodisintegration are now available throughout the energy region sensitive to the NA force. Static-NN coupled-channel calculations are in good agreement with the new data taken in parallel kinematics but fail to reproduce the perpendicular polarization state. The inclusion of retardation, particularly in the π -MEC, and possibly an explicit treatment of 2π -channels, may be some of the more hopeful avenues to reconciling theory and experiment.

THE DRELL-HEARN-GERASIMOV SUM RULE AND SPIN POLARIZABILITY OF THE NUCLEON

A new phase of LEGS, with experiments beginning in 1996, will focus on measurements of double-polarization observables. This will involve a order of magnitude increase in the complexity of experiments and the associated instrumentation. The new collaboration responsible for the development of this phase - the LSC, or LEGS-Spin Collaboration - consists of ~45 physicists (including 7 graduate students) from BNL, seven US Universities - (Christopher Newport, Norfolk State, Ohio, South Carolina, Syracuse, Virginia Polytechnic Institute & SU, and Virginia), and five European institutions (Frascati, Genova, Gießen, IPN-Orsay, and Rome-II). The new experiments will utilize the highly polarized LEGS photon beams and SPHICE, a frozen-spin hydrogen and deuterium target. An ~80% 4π detector for neutrals and charged hadrons, SASY (the Spin ASYmmetry array) will be constructed for these measurements. A drawing of SASY and SPHICE is shown in Figure 3. Much of 1996 will be devoted to preparing for this new phase of activity. SPHICE represents an innovative new technology for polarized targets and its fabrication requires considerable preparation. First targets should be available at the beginning of 1997. Installation of the "core" elements of the SASY detector - large arrays of NaI(Tl), Lead Glass, and Plastic Scintillator - will take place early in 1996. The full design, including a superconducting solenoidal magnet and a Time Projection Chamber, will be installed by the end of 1997.

SPHICE, a Strongly Polarized Hydrogen and Deuterium ICE Target, represents a new technology utilizing molecular HD in the solid phase. The coupling between the nucleon spin and the atomic lattice, which is primarily through molecular rotations, causes the spin alignment to relax back to the unpolarized state. This represents the chief limitation on conventional "frozen-spin" targets. However, the heteronuclear HD molecule, consisting of non-identical particles, does not have any restrictions on the orbital and spin angular momenta and hence can be in

the molecular-rotation state $J=0$, independent of the H or D spin orientations at low temperature. Thus, the spin-lattice coupling, and the corresponding relaxation rates, are exceedingly small and imply a sample whose spins would remain "frozen" for many days even at 4°K.

The forward Compton cross section for initial and final photon polarizations ϵ and ϵ' has been given by Gell-Mann, Goldberger and Thirring as,

$$A(\omega) = f(\omega^2) \epsilon \cdot \epsilon' + i\omega g(\omega^2) \vec{\sigma} \cdot (\epsilon \times \epsilon')$$

where σ is the target spinor. The spin independent, $f(\omega^2)$, and spin dependent, $g(\omega^2)$, amplitudes can be expanded in a Taylor series,

$$f(\omega^2) = f(0) + f'(0)\omega^2 + O(\omega^4)$$

$$g(\omega^2) = g(0) + g'(0)\omega^2 + O(\omega^4)$$

where the prime-symbol indicates differentiation with respect to ω^2 . Here, $f(0)$ is the Thomson scattering limit that corresponds to oscillating the nucleon up and down with the electromagnetic field of the photon. $f'(0)$ is identified with the sum of the electric and magnetic polarizabilities of the target and measures how the constituents of the target rearrange themselves in response to the applied electromagnetic field. In analogy, $g'(0)$ is referred to as the spin-dependent polarizability of the nucleon. The GGT dispersion relations provide a sum rule for this spin polarizability (γ),

$$\gamma \equiv g'(0) = \frac{1}{4\pi^2} \int_0^\infty \frac{\sigma_{1/2} - \sigma_{3/2}}{\omega^3} d\omega$$

Here $\sigma_{1/2}$ and $\sigma_{3/2}$ are the total reaction cross sections measured with the photon helicity oriented opposite to the nucleon polarization or parallel to it, respectively. Another GGT dispersion relation can be written down for $g(0)$,

$$g(0) - g(\infty) = \frac{1}{4\pi^2} \int_0^\infty \frac{\sigma_{1/2} - \sigma_{3/2}}{\omega} d\omega$$

Low, Gell-Mann and Goldberger (LGG) have evaluated $g(0)$ in terms of κ , the anomalous magnetic moment of the target,

$$g(0) = -\alpha\kappa^2/2m^2$$

Drell and Hearn, and independently Gerasimov (DHG), have noted that under the assumption $g(\infty)=0$, a sum rule is obtained that relates these polarized reaction cross sections to the anomalous magnetic moment of the target,

$$DHG = \int_0^\infty \frac{\sigma_{1/2} - \sigma_{3/2}}{\omega} d\omega = -\frac{2\pi^2\alpha\kappa^2}{m^2}$$

In a recent work by members of this group, [*Phys. Rev.*, D50, R6681, (1994)], these integrals have been evaluated using the FA93 photo-pion multipole analysis of the VPI group to predict the spin dependent cross sections. This multipole set extends out to 1.7 GeV, and

the integrals appear to have converged above about 1.2 GeV. The result of these calculations for the average of the proton and neutron sum rules are summarized in Table 1. (In the literature the DHG sum rule is usually broken up into vector, V, scalar, S, and mixed vector-scalar, VS, components. The proton-neutron average corresponds to the VS sum rule.) The FA93 prediction of $-225 \times 10^{-4} \text{ fm}^2$ (or μb) for DHG_{V+S} shows impressive agreement (2.7%) with the value expected from the anomalous magnetic moments, $-219 \times 10^{-4} \text{ fm}^2$. For the spin polar-

izability, comparisons can be made with Chiral perturbation theory. Relativistic-calculations for γ have been reported that include all diagrams to the one-loop order, excluding those involving a delta. The delta effects are large, and they have estimated the contributions from the dominant diagrams. The result, $-98 \times 10^{-6} \text{ fm}^4$, is within 14% of the FA93 evaluation. This is very encouraging agreement, although the final word must await a calculation which includes all delta contributions to the same order.

Table 1: Multipole predictions for the γ and DHG sum rules on the proton + neutron, compared with chiral perturbation theory predictions for γ and with the magnetic moment predictions for DHG.

	χPT	FA93 (VPI-SAID)	$-(\kappa_p^2 + \kappa_n^2) \frac{2\pi^{2\alpha}}{m^2}$
$\gamma_{V+S} = 1/2(\gamma_p + \gamma_n)$	$-98 \times 10^{-6} \text{ fm}^4$	$-86 \times 10^{-6} \text{ fm}^4$	
$\text{DHG}_{V+S} = 1/2(\text{DHG}_p + \text{DHG}_n)$		$-225 \times 10^{-4} \text{ fm}^2$	$-219 \times 10^{-4} \text{ fm}^2$

Since in χPT the delta contributions for the neutron and the proton are the same, the uncertainties in the one-loop calculation disappear when we consider the difference, $1/2(\text{proton} - \text{neutron})$. These results are summarized in Table 2. Now, the relativistic one-loop value for γ is in impressive agreement with the FA93 evaluation. However, in sharp contrast, the predictions for γ are very different from the magnetic moment values – both in sign and a factor of 4 in magnitude.

Table 2: Multipole predictions for the difference sum rules, $1/2(\text{proton} - \text{neutron})$, compared with chiral perturbation theory predictions for γ and with the magnetic moment predictions for DHG.

	χPT	FA93 (VPI-SAID)	$-(\kappa_p^2 - \kappa_n^2) \frac{2\pi^{2\alpha}}{m^2}$
$\gamma_{V+S} = 1/2(\gamma_p - \gamma_n)$	$-52 \times 10^{-6} \text{ fm}^4$	$-48 \times 10^{-6} \text{ fm}^4$	
$\text{DHG}_{V+S} = 1/2(\text{DHG}_p - \text{DHG}_n)$		$-65 \times 10^{-4} \text{ fm}^2$	$+15 \times 10^{-4} \text{ fm}^2$

The results in Table 2 are quite puzzling. In principle, the different energy weightings of the integrals admit the possibility that contributions above the 1.7 GeV limit of the VPI data base could bring the value up to that expected by the sum-rule, without appreciably affecting. However, 1.7 GeV is already so large that such differences would have to be huge in order to overcome the energy weighting. For example, 200 mb between 2 and 3 GeV, which would require a prominent

but as yet unidentified resonance; or a constant level of -20 mb extending out to 100 GeV, which would be much larger than the contributions of the resonance region in which the isospin structure of the D and N^* states can be expected to enhance the proton-neutron difference. Apart from such scenarios, which seem highly unlikely, there are only two other possibilities. Either a) both the two-loop corrections to the spin polarizability are large and the existing multiples are wrong, or b) modifications to the

DHG sum rule are needed to fully describe the isospin structure of the nucleon.

It is possible that the two-loop corrections to the calculations for γ are large. Although this is not usually the case for expansions, it would not be without precedence. This would imply that the multipoles would have to be modified. Changing the multipoles would potentially affect the predictions for a variety of observables. Although it is possible to imagine complicated alterations that would leave cross sections and single-polarization observables largely unaffected, several double-polarization observables would have to change significantly. As yet, there are no measurements of these quantities.

Alternatively, if the multipoles are basically correct, then the DHG sum rule requires at least a modification of the form,

$$DHG_{NS} \rightarrow DHG_{VS} - C$$

and the simplest choice for the correction factor would be $C=2\pi^2[g_p(\infty)-g_n(\infty)]$, with $g_p(\infty) \approx -g_n(\infty) 2\mu_b$. In other words, contrary to the original DHG assumptions, g_p and would tend to nearly equal but opposite constants at high energy. The physical origins of such constants would be quite interesting, although other choices for have also been proposed. The DHG_{VS} integral is just the $Q^2 = 0$ limit of the Bjorken sum rule integral, and $C=0$ has been assumed in modeling its Q^2 evolution. The Q^2 dependence of a possible non-zero $g(\infty)$ remains to be considered.

This is a challenging question that will be pursued in planned experiments at many different laboratories. Since the key physics issues with the least model dependence are in the proton-neutron difference, each of which involves cross section differences themselves, considerable care must be taken by the experimenters to minimize systematic uncertainties. The approach at LEGS is to carry out the proton and neutron measurements simultaneously with the new polarized target, SPHICE.

SCATTERING AND CRYSTALLOGRAPHY STUDIES OF BIOLOGICAL MATERIALS

Lonny Berman
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HOLOGRAPHY

In x-ray holography, the wavefield diffracted by a specimen is mixed with a reference wave to encode its amplitude and phase in a hologram. A team including S. Lindaas and M. Howells from Lawrence Berkeley National Laboratory, and C. Jacobsen and S. Spector from SUNY at Stony Brook, has used the coherent soft x-ray beam from the X1A undulator beamline to record in-line holograms on photo resists. The developed photo resist encodes the x-ray intensity distribution as a surface relief pattern on photo resist. Thus, the hologram, which has no inherent magnification, is well suited to being recovered by using a specially-built, linear field atomic force microscope to "read" the photo resist. The image is then

reconstructed by Fresnel transformation of the digitized hologram in a computer (iterative algorithms are also under development for reduction of the so-called "twin image" present in these in-line holograms). By this approach, 40 nm resolution images of fibroblasts have been obtained, and experiments will soon begin aimed at recording holograms of frozen-hydrated specimens using a cryo-holography system.

MACROMOLECULAR CRYSTALLOGRAPHY

On beam line X4A, 12 new MAD (multiwavelength anomalous dispersion) phased structures were published in the past year (see X4A publication list). The method was extended by the assortment of elements now being used for MAD experiments. Of the structures reported, 8 were heavy atom derivatives (6 Hg, 1 Yb, and 1 U), 3 selenomethionine-substituted, and the final one a Zn-containing protein. The energy range for experiments was extended to the $U_{M_{IV}}$ edge at 3.728 keV (3.326 Å) (Y. Liu and W. Hendrickson, unpublished) at the low energy end to the $U_{L_{III}}$ edge (17.17 keV, 0.72 Å) at the high energy end. At the low energy end, the experimenters showed the feasibility of exploiting the large (80 electron) anomalous signal. In the $U_{L_{III}}$ edge experiment, the structure of the cell surface adhesion molecule cadherin was determined (L. Shapiro, A.M. Fannon, P.D. Kwong, A. Thompson, M.S. Lehmann, G. Grubel, J.-F. Legrand, J. Als-Nielsen, D.R. Colman, and W.A. Hendrickson, *Nature*, 374, 327-337, [1995]).

During the past year, data collection for MAD experiments on beamline X12C has become essentially automatic. The user prepares a script to define the data collection, including the use of the "Friedel flip" to measure Bijvoet pairs

Figure 2 X12C: The solvent-accessible surface area of the outside (a) and inside (b) of the TYMV virion as visualized by GRASP (A. Nicholls, K. Sharp, and B. Honig, *Proteins*, 11, 281-296, [1991]). The virion is made up of 180 copies of the 21 kD coat protein, arranged icosahedrally. The pentameric and hexameric units of coat protein are nearly indistinguishable on the outside of the virion, but are very different on the interior.

if necessary; then, the software takes over. At each wavelength change, the absorption spectrum of the heavy atom is measured, the feature of the spectrum that defines a data collection wavelength (inflection point, peak, etc.) is analyzed, the monochromator is set to that feature, and data collection proceeds. Several MAD structures have been solved with this method.

An exciting result from X12C, that was made possible by its versatile kappa diffractometer, was the direct solving of a 450-atom structure. This was the α_1 peptide, solved by G. Privé of the University of Toronto and D. Eisenberg of UCLA. This peptide was designed to form an alpha helix and to self-assemble into a four-helix bundle. Data were taken from a crystal of the peptide to a resolution of 0.92 Å while it was kept frozen at 100 K. The structure was solved by the direct method known as "shake-and-bake," developed by the Hauptman group in Buffalo. The resulting structure shows four antiparallel helices. A representative electron density map from this structure, revealing the atoms of a leucine residue, is shown in Figure 1.

One of the classic structures in all of structural biology has been turnip yellow mosaic virus (TYMV), having been studied for over 50 years. In the 1960s, Caspar and Klug determined its surface structure in some of their earliest work on reconstruction of viruses from electron micrographs. In work done by M.A. Canady, A.

McPherson, and co-workers from the University of California at Riverside, the structure of this virus has been solved to 3.2 Å resolution, using techniques that have become standard for virus crystallographers (isomorphous replacement and molecular averaging). Many of the data used to solve the structure were measured at X12C. Use of the long working distance and 2 θ -angle tilt of the X12C diffractometer allowed data to be collected to 3.0 Å resolution, even with one of the unit-cell edges being over 500 Å.

The overall structure of TYMV is similar to that of other spherical viruses, with the surface of the virion displaying very prominent protrusions at the icosahedral fivefold and pseudo-sixfold axes (see Figure 2). These protrusions correspond to the pentameric and hexameric units of the coat protein (Figure 3). The structure of the monomer has the same so-called jellyroll fold as the plant viruses and several animal viruses such as polio and the common cold (Figure 4). TYMV is an interesting model for study of virus assembly because it has unusually strong protein-protein contacts. Also, it is able to release its RNA *in vitro*; it loses a pentamer or hexamer from the protein capsid. The research team predicts that it is most likely a pentamer that leaves, uncorking the virus to allow RNA release, since the pentamer makes fewer contacts with the protein capsid. This finding will lend insight to the study of the viral life cycle in infected cells with the prospect of

Figure 3 X 12C: The pentameric (3a) and hexameric (3b) units of the TYMV capsid. The primary structure of the monomers is identical, but because they are placed in different environments in the capsid they each have a slightly different conformation. This is most evident at the N terminus, which crosses under the hexameric units but is disordered at the pentamer. This figure was generated using MOLSCRIPT, described by P.J. Kraulis, *J. Appl. Crystallogr.*, 24, 946-950, [1991]].

saving the lives of turnips worldwide.

Turning to another MAD experiment, the structure of a specific complex between the p50 subunit of the transcription factor NF κ B and DNA was solved using X25 and X4A, by C.W. Müller, F.A. Rey, M. Sodeoka, G.L. Verdine, and S.C. Harrison of the Howard Hughes Medical Institute and Harvard University (work reported in *Nature*, 373, 311-317, [1995]). In particular, the very high intensity available at X25 was essential to the success of this project. Three orthogonal views this complex are shown in Figure 5 (see Section Divider on page 8). The p50 protein (365 amino-acid residues in the form shown here) binds to DNA as a dimer. Its polypeptide chain (represented as a ribbon) folds into 2 domains (colored yellow and red). The amino-terminal domain (yellow) contains most of the segments that interact specifically with DNA; the carboxy-terminal domain (red) mediates dimerization. The DNA (blue) contains 11 base pairs.

LAUE DIFFRACTION CRYSTALLOGRAPHY

Recent work on X26C by B. Stoddard of the University of Washington involved the trapping of steady-state intermediates by the clever choice of site-directed mutants. The reaction investigated was that catalyzed by isocitrate dehydrogenase (IDH). The reaction proceeds in two steps. The first is the transformation of isocitrate

to oxalosuccinate, an intermediate that had never actually been observed before this experiment. The second is conversion of this to α -ketoglutarate. Each of these is catalyzed by a different portion of the enzyme. The workers were able to prepare site-directed mutants of the enzyme that blocked first one, then the other step of the reaction. Then they determined the structure of the intermediate states of the enzyme through use of the Laue diffraction method. Crystals of both mutants of IDH were mounted in flow cells. Diffraction data were taken first on the apo-enzymes, i.e. with no substrate nor cofactors present in the solution. Then the reactants were flowed into the cell and full three-dimensional data were taken. The species that were to be observed should represent a steady-state accumulation of intermediates of the reaction. The importance of using this rapid method for data collection was that the crystals themselves were not stable in the presence of the reactants—only a short time was available to take the data before the crystals fell apart.

The results of the two experiments are revealed in Figure 6. On the left is shown the accumulation of the reactants NADP $^{+}$ towards the bottom and isocitrate complexed to a magnesium ion at the top and towards the rear. Accumulation of the supposed intermediate oxalosuccinate is revealed in the right hand side of the figure. The dramatic difference that is seen between the

Figure 4 X12C: The monomer of the TYMV capsid. The fold of the TYMV monomer is the canonical jellyroll fold, an 8 stranded β sheet. This fold has been found in almost every virus structure solved to date. The finding that the N terminus was interior to the virus was surprising, since immunological work had placed it on the exterior. The TYMV coat protein is unique in that it has an unusually high number of prolines (10.5% of the residues). Very few prolines are found in the ordered secondary structure; rather, they are concentrated at the ends of the β sheets, at the beginnings of the helices, and mostly in the outer loops. This figure was generated using MOLSCRIPT.

two halves of the figure arises from the loss of electron density in the portion of the NADPH molecule that includes the nicotinamide ring and its phosphate backbone. This structure confirms nicely the appearance of the oxalosuccinate intermediate, which had only been proposed before this experiment.

The author wishes to acknowledge the contributions to this section by Stephen Harrison (Harvard U.), Chris Jacobsen (SUNY@Stony Brook), Craig Ogata (Howard Hughes Medical Institute) and Bob Sweet (BNL - Biology).

Figure 6 X26C: See text for description.

SCIENCE

TIME RESOLVED SPECTROSCOPY

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I. INTRODUCTION

The promise of using the pulsed nature of synchrotron radiation (SR) for time-resolved investigations, envisaged since the inception of dedicated storage rings, is being fulfilled by a stable community of users at NSLS. A wide variety of experiments, encompassing the full range of available photon energies, from far-infrared to hard x ray, are presently carried out on gases, liquids, solids, and surfaces. The time domain ranges from subnanosecond, limited by the synchrotron pulse duration, to 100's of nanoseconds, limited by the synchrotron interpulse period. These parameters depend on which of the two rings at NSLS, the X-Ray or the VUV, is employed and are listed in Table 1.

Most pulsed, time-resolved studies require that only one electron bunch circulate in the X-Ray (VUV) Ring rather than the usual 25 (7). The need for only one bunch (1-B) depends on the experiment. For example, the longer time window available between SR pulses in 1-B fills (see Table 1) may be necessary to record long time decays. Similarly, a long time window circumvents overlapping photoion time-of-flight spectra. Finally, the number of photons per pulse increases in 1-B operations, by factors of ~3 on the VUV Ring and ~10 on the X-Ray

Ring, with a concomitant improvement in signal for experiments with duty-factor limitations imposed by detectors or, in the case of some pump-probe studies, by low pump-laser repetition rates. The 1-B fills are scheduled for only limited periods to ameliorate the impact on other users caused by the reduced lifetime and injected current. The X-Ray Ring is formally scheduled ~ 10 days of 1-B operations per year. Timing operations on the VUV Ring are scheduled with less formality: 8 or 10 shifts, dependent on day of week, are requested a week in advance.

Highlights of work performed on each ring are presented below.

II. VUV RING

U9B

The time-dependent fluorescent emission from biological molecules reveals important information on their photophysical and structural properties. Most biological molecules begin absorbing only in the UV, requiring excitation with pulsed synchrotron radiation if conve-

Table 1: NSLS Storage-ring characteristics relevant to time-resolved experiments.

	Radio Frequency (RF)	Maximum number of bunches	Minimum interpulse period	Maximum interpulse period (single bunch)	Nominal pulse duration (FWHM)
VUV Ring (750 MeV)	53 MHz	9	19 ns	170 ns	1.5 ns (a)
X-Ray Ring (2.5 GeV)	53 MHz	30	19 ns	566 ns	0.6 ns (b)

(a) With 4th harmonic cavity powered, trapezoidal profile. Pulse lengths of 200 ps (calculated) expected in future special operations.

(b) Single bunch, 90 mA beam current.

nient tunability of the excitation energy is desired. When performed with photon energies less than the 7-eV water cutoff, fluorimetry is a desirable approach since natural aqueous environments may be employed. John Sutherland (BNL-Biology) and coworkers have been examining biological molecules such as peptides (protein building blocks) for some time using a fluorimeter capable of measuring the time decay of fluorescence and its polarization at preselected fluorescent wavelengths.

Until recently, mapping out the wavelength dependence of the fluorescence decay time required time-consuming accumulations for each discrete wavelength, leading to inevitable gaps in emission wavelength and often necessitating that spectral resolution be compromised in order to reduce the time for each

accumulation. As described in last year's NSLS Activity Report, this is no longer the case with the commissioning of a new fluorimeter, capable of measuring the time decay spectrum *simultaneously* with an entire emission spectrum. The instrument uses a two dimensional histogramming memory to associate the time of arrival of a fluorescent photon, detected with a microchannel plate (MCP) at the output of the fluorescence spectrometer, with the photon's position, detected with a position-sensitive anode placed after the MCP and over which the emission spectrum is dispersed.

In the past year, a new capability was added which enables the measurement, also simultaneously, of changes in the polarization anisotropy of fluorescent emission. When a rigid molecule is excited with linearly polarized light, it fluoresces predominantly with the same polarization. However, since motion of the molecule after excitation will reorient the transition dipole, monitoring the fluorescence polarization both parallel and perpendicular

Figure 1 U9B: Example of fluorescence excited by synchrotron radiation pulses of 290-nm wavelength as obtained with the new fluorimeter on U9B. The fluorescent intensity is resolved *simultaneously* into time t (after excitation), wavelength λ , and polarization. The data for fluorescence polarization parallel ($\lambda_{||}$) and perpendicular ($\lambda_{\perp}$) to the exciting synchrotron radiation polarization are displayed as separate relief plots of intensity I vs. t and λ . The seven distinct time spectra correspond to the seven bunches in the ring at the time of the measurement. The sample is outer surface protein A (Osp A), a major antigen of the Lyme disease bacterium, in water at 6° C. This protein contains a lone tryptophan fluorophore, which is believed to initiate a conformation change once it absorbs. The data suggest that the new conformation does not include a rotation of the tryptophan residue since the transition-dipole moments do not reorient in time, i.e., $I_{\perp}$ does not grow at the expense of the initially populated moments which emit predominantly with $I_{||}$. The efficient data rates from the new instrument will provide detailed dynamical information on biological molecules. (Lisa A. Kelly, John Trunk, Junyan Shi, and John C. Sutherland).

to that of excitation provides a unique means of assessing, for example, time-dependent protein conformational changes. To obtain the polarization information simultaneously, a Wollaston (double deviating) prism was introduced into the fluorescence optical train in order to separate the propagation directions of the two polarizations away from each other. This has the effect of producing two different wavelength spectra, one for each polarization direction, with one displaced above the other on the 2-dimensional position-sensitive anode at the output of the spectrometer. The fluorimeter thus now records in a four-dimensional space: fluorescence intensity I vs. time, wavelength, and polarization.

Figure 1 illustrates results obtained, *in aqueo* at 6° C, from the lone tryptophan component of outer surface protein A (Osp A), a major antigen to the bacterium responsible for Lyme disease. The time axis encompasses one round-trip time of the VUV Ring, which was operating in 7-bunch mode so that seven distinct emission

spectra, one for each pulse, appear. Fluorescence anisotropy is evident since $I_{||} > I_{\perp}$. It is generally believed that a protein such as Osp A exhibits a conformational change in response to tryptophan photoexcitation. If as a result the tryptophan itself were to rotate, a time-dependent anisotropy would be observed, which these preliminary data suggest is not the case.

U13UA

The many-body problem is pervasive in all of physics. In fact, it is not too much of an exaggeration to say that the lack of an exact solution to even the three-body problem is at the root of most theoretical attempts at understanding physical phenomena.

Helium is the simplest atomic three-body system, and therefore the simplest which can exhibit electron-electron correlation. As a result, photoionization of helium has long been used as a testing ground for understanding correlation phenomena, such as autoionization, correlation-satellite production (shakeup) and double photoionization. At higher photon energies, Compton scattering can produce single or double ionization of helium with a cross section which dominates that of photoionization. Theoretical prediction of the energy dependence of the double photo- or Compton ionization of helium is a fundamental problem in atomic physics which requires solution of the Coulomb three-body problem.

At low energies (the double-ionization threshold is at 79 eV), many measurements have been made of the ratio of helium double to single photoionization cross sections. Recent theories which relate the ratio due to energetic charged particle impact, which is well-established experimentally, to that following photoionization near threshold, have concluded that the existing low-energy measurements are systematically high. Jon Levin and co-workers have made helium ion time-of-flight measurements on U13UA extending from threshold to 700 eV which are consistently below earlier measurements and in better agreement with theory (Figure 2).

III. X-RAY RING

During single-bunch operations, at least four research groups conducted timing experiments on as many beamlines during 1995, with several groups working on more than one line. Historically, some beam lines have been used extensively during 1-B operations, and have even become oversubscribed. The result is that some groups perform experiments on several lines in order to obtain access to the relatively limited 1-B time.

X24A

During the first beam time of a new proposal by Ralf Wehlitz (working with Letitia Pibida, Jon Levin and Ivan Sellin, U. Tennessee), electron spectra as well as electron-electron coincidence spectra have been obtained around the argon K edge. Monochromatized synchrotron light intersected an effusive gas beam and electrons coming from this interaction region were detected with a cylindrical mirror analyzer (CMA) and a time-of-flight (TOF) spectrometer. The TOF spectrometer, whose use requires the availability of 1-B operations, and the CMA were mounted horizontally in a plane perpendicular to the photon beam. The CMA was equipped with a position-sensitive anode, thereby permitting measurement of the electron angular distribution. In order to detect electrons of low kinetic energies, the chamber was covered with μ -metal on the inside. The electron spectra taken on the Ar 1s-4p resonance reveal a complex structure of low kinetic energy Auger lines (particularly around 5 eV) not seen

Figure 2 U13UA: Near-threshold ratio of double to single photoionization of helium using monochromatic undulator radiation on U13UA (solid circles and solid triangles, present results) compared with available theory, as indicated, and published experimental results (from Jon C. Levin, G. Bradley Armen, and Iran A. Selling, *Phys. Rev. Lett.*, in press).

Figure 3 X24A: L-MM Auger lines in coincidence with the $K-L_{2,3}L_{2,3}$ Auger line on the $Ar\ 1s \rightarrow 4p$ resonance. The dotted line corresponds to the non-coincident spectrum of the same Auger group arbitrarily scaled to the coincident spectrum.

before. However, the intensity is too low for a detailed analysis of these Auger lines yet, but will be part of future investigations. The main goal of these investigations was to record the Ar L-MM Auger lines in coincidence with one K-LL Auger line to disentangle the complex structure of the L-MM Auger group. While the CMA was tuned to the $K-L_{2,3}L_{2,3}$ Auger energy, the group of L-MM Auger lines was detected with the TOF spectrometer. The coincident L-MM Auger spectrum shows a different structure than the corresponding non-coincident spectrum because of the decay-path selection in the first step (Figure 3). Further studies will include other "first-step" Auger lines (e.g. K-LM) and the angle correlation between the two outgoing Auger electrons. See also X24A Experimental Abstracts in this volume.

X24C

Photoelectron spectroscopy is extended from a probe of the ground state to one of the excited state through pump-probe photoemission. In this technique, a laser pulse first excites (i.e. pumps) electrons into normally unoccupied levels and a second UV pulse, incident with controlled delay relative to the laser pulse, photoemits from the excited electron population. In this way the energies, wave vectors, and population dynamics of excited states are accessible directly. The technique is usually practiced with laser-based UV sources on metals and semiconductors. However, Jim Long (Naval Research Lab) and coworkers have extended the technique to include the use of synchrotron radiation and, most recently, to examine non-traditional materials such as the fullerene C_{60} .

Figure 4 displays results obtained from a 420 Å film of C_{60} deposited *in situ* on a copper substrate and subsequently photopolymerized at room temperature by exposure to copper-vapor laser pulses ($h\nu=2.43$ eV, 5-ns FWHM). The inset displays the photoelectron spectrum of excitons excited in the film, held at 84 K, by the same laser. For this spectrum, the laser pulses were overlapped in time with the synchrotron radiation pulses ($h\nu=8.5$ eV, 0.6 ns FWHM). Single-bunch operations maximized the number of synchrotron-radiation photons coincident with the laser pulses, which had a repetition rate of 6 kHz, much less than the synchrotron rate of 1.8 MHz (single bunch). The center energy of the exciton band lies below the band gap of solid C_{60} , reflecting the energetics of exciton binding, lattice relaxation, and, possibly, trapping at defects.

Exciton dynamics governs efficiencies for phenomena as diverse as photochemical reaction, energy transfer, nonlinear optical properties, and triplet and free radical formation, and can also yield other information about the state of a sample. In many systems, singlet excitons decay into lower-energy triplet excitons through intersystem crossing and thus a full dynamical knowledge requires tracking both singlet and triplet populations. Optical techniques, such as transient absorption or photoluminescence, are valuable dynamical probes but, in general, cannot form a complete picture because any one experiment exhibits vastly different detection sensitivities for singlet and triplets. In contrast, photoelectron spectroscopy enjoys equal detection sensitivities. The decay dynamics of the exciton populations in photopolymerized C_{60} films were examined by monitoring the strength of the

peak in the photoelectron energy spectrum (vertical line in the inset) as a function of the relative time between laser and synchrotron radiation pulses.

In Figure 4, the microsecond decays were measured in 25-bunch operations because long gate times could be used to integrate the signal over many synchrotron pulses without distorting the decay profile; the nanosecond data (filled circles) necessitated single-bunch operations. Triplet excitons comprise the long-lived component, which is found to be consistent with exponential decay. At shorter times after the laser pulse, the decay is complicated by higher-order (e.g. bimolecular) kinetics due to the large ($\sim 10^{19} \text{ cm}^{-3}$) exciton density. Coupled rate equations describing singlets, triplets, and free carriers, when integrated and fitted to the data, strongly suggest that both triplets and singlets contribute to the signal at early times. The singlet population converts to triplets through intersystem crossing (1 ns) and bimolecular processes. Further analysis, including comparison of the different kinetics observed for polymerized and pristine (not shown) films, should yield new insights into exciton dynamics in molecular and polymeric solids.

X25

Despite the fundamental importance of the problem, theoretical predictions of the ratio of double-to-single ionization of helium by high-energy photons have not converged (they vary by a factor of two). Jon Levin (with Brad Armen and Ivan Sellin, U. Tennessee) have conducted an ongoing program of research aimed at elucidating the roles of photoionization and Compton ionization in the 5-10 keV region, over which energy range Compton ionization gradually supplants photoionization as the dominant ionization mechanism, and

Figure 4 X24C: Photoelectron spectrum (inset) of excitons excited in a photopolymerized film of C_{60} by a 5-ns copper-vapor laser pulse and probed by a time-overlapped synchrotron pulse. Vertical bar denotes the energy, relative to the center of the highest occupied molecular orbital (HOMO), at which the time-dependent data in the main portion of the figure were taken. Numerical modelling strongly suggests that the data at short times (solid circles), taken in single-bunch mode, comprise both singlets, which decay within a few nanoseconds, and the long-lived triplets into which the singlets and free carriers convert. The kinetics are strongly influenced by the nonlinearities introduced by conversion scattering among the singlet, triplet, and free-carrier populations. The presence of triplets is confirmed by the long lifetimes (10-20 μs) observed during 25-bunch operations (solid curve). (S. Chase, J. P. Long, R. Klaffky, W. R. Hunter, and M. N. Kabler).

Compton ionization alone from 10-20 keV. Single-bunch operations are critical for these measurements, which use the ring timing signal to differentiate between singly and doubly charged helium by time-of-flight methods. Time-of-flight techniques which require detection of an ejected electron can introduce systematic biases, and pulsing of extraction fields produces broad ion time-of-flight peaks, making discrimination against large-cross-section electron-impact ionization difficult.

Because of the small double-ionization cross section ($\sim \text{mbarns}$ at 20 keV), and low gas-phase target number density, the intense wiggler radiation available at X25 has proven crucial. Results to date have helped to differentiate among the several theories currently available (see X25 Experimental Abstracts in this volume).

UV PHOTOEMISSION AND SURFACE SCIENCE

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VALENCE BAND PHOTOEMISSION AND RESONANT PHOTOEMISSION

Recently $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (A = Sr, Ca, Pb etc.) have attracted a great deal of attention because of the technological implications of their large magnetoresistance as well as the intriguing phase transitions associated with magnetoresistance in this class of materials. High resolution valence band photoemission and resonant photoemission have been used to reveal the electronic structure changes associated with the ferromagnetic transitions in $\text{La}_{1-x}(\text{Ca,Pb})_x\text{MnO}_3$ by J.-H. Park, C.-T. Chen, S.-W.

Cheong, W. Bao, G. Meigs (AT&T Bell Labs), V. Chakarian and Y. U. Idzerda (NRL) at beamline U4B. As shown in Figure 1(a), the overall valence band photoemission spectra from both $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ exhibit no changes with temperature. However, near the Fermi level, as shown in Figure 1(b), a metallic Fermi edge clearly emerges with decreasing temperature for both samples. These data provide strong evidence that the ferromagnetic transition is closely related to a metal-insulator transition. To further investigate the microscopic origin of this paramagnetic-insulator-to-ferromagnetic-metal phase transition, the authors also performed resonant photoemission near the Mn 2p absorption edge to enhance the Mn 3d contribution to the valence band. With decreasing temperature, an energy shift of 0.2 eV was observed for the lowest binding energy state, 4A_2 . From these findings, it is argued that the physical origin of the phase transition lies in the close interplay between the charge fluctuation energy for electron hopping from the Mn^{+3} site to the Mn^{+4} site, and the spin-dependent electron hopping energy.

Angle-Resolved Photoemission of Novel Materials

The electronic structure of low dimensional oxide conductors, organic superconductors, and wide band gap semiconductors is being studied using angle-resolved photoemission (ARP) by Kevin Smith and his group from Boston University using beamline U4A. Concerning the properties of the low dimensional oxides, the highlight of the year was the measurement of the full Fermi surface in $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$, a two dimensional conductor. A representative set of ARP spectra is shown in Figure 2, while the full Fermi surface is presented in Figure 3. Although primarily two-dimensional (2D) in nature, $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ displays numerous characteristics of a 1D conductor, in particular charge density waves and periodic lattice distortions. The explanation put forth for this by Whangbo, *et al.* [(*Science*, 252, 96 (1991))] was that the material

Figure 1 U4B: High-resolution temperature-dependent photoemission spectra of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (left panels) and $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ (right panels) taken at 110 eV photon energy: (a) wide range scans, (b) region near the Fermi level, and (c) Mn 2p_{3/2} edge on-resonant spectra.

possessed so-called hidden Fermi surface nesting. Hidden Fermi surface nesting is where a true 2D Fermi surface can be viewed as a combination of quasi-1D Fermi surface structures, all of which can be linked by one nesting vector. Most of the Fermi surface in Figure 2 can be constructed from two sets of parallel 1D Fermi surfaces, running parallel the diagonals of the rectangular surface Brillouin zone. This measurement is the first direct confirmation of the validity of hidden Fermi surface nesting, a widely cited mechanism used to explain quasi-1D phenomena observed in quasi-2D systems.

Angle-resolved photoemission is also being used by Ph. Hofmann (ORNL) and E. W. Plummer (U. Tennessee) at beamline U12 to study the electronic structure of the $\text{Be}(10\bar{1}0)$ surface, and by X. Xu, R. G. Jordan and S. L. Qiu (Florida Atlantic U.) at beamline U4A to study the surface electronic structure of CuAu.

Figure 3 U4A: The measured Fermi surface for $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$.

Figure 2 U4A: Angle-resolved photoemission spectra at 18 eV photon energy from $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ as a function of detection angle.

Spin Polarized Valence Band Photoemission from Magnetic Surfaces

Photoemission studies of the quantum well states on Co, Ni and CoNi alloy substrates have been performed by a group from the BNL Physics Dept. (D.-J. Huang and P. D. Johnson). In several studies of noble metals deposited on ferromagnetic substrates, it has been shown that "quantum well" states exist, that they reflect the finite layer thickness, and that these states are highly spin polarized. As the thickness of the noble metal film increases, these states cross the Fermi surface with a frequency identical to that observed for the exchange coupling in the associated multilayers. These observations, taken together, lend support to the idea that the quantum well states mediate the coupling in the magnetic multilayers. Photoemission spectra recorded at $k_{\parallel}=0.765 \bar{\Gamma}\bar{X}$ from Cu films deposited on Co(001) exhibit a small peak near the Fermi level with a thickness-dependent intensity modulation of approximately 3 layers, corresponding to spanning vectors at the neck of the copper Fermi Surface "dog bone". A periodicity of three layers is close to that observed for oscillatory exchange coupling in the associated magnetic multilayers. Quantum well states at the center of the surface Brillouin in Cu films deposited on CoNi alloy substrates have also been identified. These states are less intense and have slightly lower binding energies than those in Cu on Co(001), particularly in the vicinity of the Fermi level. This observation can be

Figure 4 U5UA: The binding energies of quantum well states at the center of the surface Brillouin zone in Cu films deposited on Ni(001) and Co(001), obtained from angle-resolved photoemission spectra excited with photons of energy 23 eV, as a function of Cu overlayer thickness. The Cu/Co(001) quantum well states (open circles [K. Garrison, Y. Chang, and P. D. Johnson, *Phys. Rev. Lett.* **71**, 2801 (1993)] and triangles [J. E. Ortega, F. J. Himpsel, C. J. Mankey, and R. F. Willis, *Phys. Rev.* **B47**, 1540 (1993)]) exhibit branches labeled by integer quantum numbers $\nu = 1, 2, 3$ from left to right. In contrast, the binding energy dispersion of the Cu/Ni(001) states (solid circles) as a function of Cu thickness exhibits an abrupt jump from the branch with quantum number $\nu=1$ to the branch with quantum number $\nu=2$. See text.

explained by the difference in electronic structure of the substrates (single element vs. alloy).

These results indicate that the degree of quantum confinement can be tuned by altering the electronic structure of magnetic substrates, for instance, by changing the relative elemental concentrations in the substrate. This in turn suggests the possibility of tuning the exchange coupling strength in the associated magnetic multilayers. Quantum well states in Cu films deposited on a Ni(001) substrate are also identified by using angle δ -resolved photoemission, and their binding energy dispersion as a function of Cu thickness exhibits an abrupt jump from the branch with quantum number $\nu=1$ to the branch with quantum number $\nu=2$, as shown in Figure 4.

This branching jump results from the dramatic change in the phase shift of the reflection at the interface, a consequence of the resonant scattering of the sp-derived quantum well states in Cu by the Ni quantized d-bands. This branching jump suggests that the quantum-well-state picture can be applied to understand the magnetic-layer dependent oscillatory coupling in these systems.

Another spin-polarized valence band photoemission study using the U5UA beamline during FY95 was that of chemisorbed Cs on Fe substrates, performed by a collaborative group consisting of D.-J. Huang (BNL Physics Dept.), E. Vescovo (NSLS), D. M. Riffe (Utah State U.), P. D. Johnson (BNL Physics Dept.), P. Abramowitz and J. L. Erskine (U. Texas Austin). In this work, spin-polarized and spin-integrated photoemission spectroscopies were used to investigate the electronic interactions between chemisorbed Cs atoms and ferromagnetic Fe films epitaxially grown on W(110). The spin-integrated Cs 5p photoemission spectra are consistent with previously observed general trends in the coverage-dependent binding energy shifts of alkali atom core-level spectra. The Cs 5p binding energy in the first atomic layer decreases as the Cs coverage increases due to dipolar repulsion and band formation. The binding energies of Cs in the second layer are smaller than those in the first layer, an indication that the Cs-Cs interaction is weaker than the Cs-Fe interaction. In addition, the lifetime width of Cs in the first layer is much larger than those in the second layer. This dramatic change of lifetime width is suggestive of s-p hybridization in the first-layer-Cs valence electrons. That no measurable spin-polarization exists in the

Cs 5p spectra suggests that there is little or no induced magnetic moment on Cs site, in contrast to the observation of an induced magnetic moment in chemisorbed oxygen and sulfur on ferromagnetic substrates. Data analysis is under way to understand the Cs-Fe electronic interactions.

Figure 5 U13UA: Sulfur 2p photoemission spectra from (A) atomic sulfur and (B) methyl thiolate (CH₃S) adsorbed on Ni(100) and Ni(111) surfaces as a function of coverage or temperature. The spectra were recorded using 250 eV excitation.

CORE LEVEL PHOTOEMISSION

Soft X-ray Photoemission from Sulphur-Containing Molecules on Metal Surfaces

The surface chemistry group from Oak Ridge National Laboratory (David Mullins, Deborah Huntley and Steve Overbury) completed a series of experiments that demonstrated a direct correlation between the sulfur (S) 2p core level binding energy and the adsorption site of the adspecies. They then applied this correlation in understanding the complex reaction chemistry of CH₃SH on Ni(111). Since an early investigation of S on W(001), it has been hypothesized that lowering the coordination of the adsorption site lowers the S 2p binding energy. The most direct way to test this hypothesis is to compare S 2p spectra for the same species on different crystal faces of the same metal. Figure 5(A) shows how the S 2p peak position shifts to lower binding energy when the S moves from a four-fold site on Ni(100) to a three-fold site on Ni(111). The S 2p peak positions at high S coverage on Ni(111) indicate that the surface has reconstructed, with some adsorption sites being the same as on Ni(100) (four-fold) and others having an even higher coordination. A similar shift in the S 2p peak positions is seen for CH₃S adsorbed on Ni(100) and Ni(111) in Figure 5(B). This

group has also performed photoelectron diffraction experiments of this adsorption system which demonstrated that, at low temperatures, CH₃S adsorbs in the three-fold site on Ni(111) and in the four-fold site on Ni(100). In the present work, a corresponding increase in the S 2p binding energy is seen between these two surfaces. When the Ni(111) surface is heated to 250K, the S 2p spectrum becomes very complex. Applying what was learned from the atomic S spectra and the CH₃S spectra at lower temperatures, it is now clear that the CH₃S is decomposing and the Ni(111) surface is reconstructing at 250K. The two S 2p_{3/2} peaks at 161.15 and 161.55 eV arise from atomic S in three-fold and four-fold sites, respectively. The S 2p_{3/2} peak near 163.30 eV results from CH₃S that has shifted into a four-fold site on the reconstructed surface.

The UC Riverside group (W.C. Simpson, J.A. Yarmoff) and the IBM group (W.H. Hung, F.R. McFeely) at beamline U8 also continued their work on the adsorption and reaction of halogens on semiconductor surfaces using core level photoemission spectroscopy.

The spin-resolved core level photoemission group from the NYU Physics Dept. [B. Sinkovic, E. Shekel (NYU) and S. L. Hulbert (NSLS)] has performed the first spin-resolved L_3 -resonant photoemission measurement using their spin-resolving electron energy spectrometer and high-flux soft x-ray photons from the U13UA beamline. The spectral distribution of this giant resonance ($2p_{3/2} \rightarrow 3d^*$) is dominated by the Auger matrix elements and is found, in the case of Fe, to closely resemble the self-convolution of the Fe valence density of states. However, the magnitude of the spin polarization is measured to be significantly higher on-resonance ($P_{on}=37\%$) than the valence band spin polarization ($P_{VB}=27\%$). These findings are consistent with a reduction of the triplet Auger matrix elements which, in turn, can be interpreted as being due to the existence of a Fermi hole, the exchange correlation responsible for keeping equal spins further apart, which effectively lowers the triplet Auger probability. This hypothesis was confirmed by measurement using off- L_3 -resonant photons, which yielded smaller spin polarization ($P_{off}=20\%$) than P_{VB} , as expected since the degree of spin polarization depends on the polarization of the initial core hole (which is different in the on- and off-resonant processes) assuming electron correlation effects are present. Thus, these measurements provide a way of studying spin-dependent electron-electron correlation in magnetic materials (see Figure 6). These results suggest that electron-electron correlations are important in itinerant ferromagnets such as Fe.

Figure 6 U13UA: Mesh surface: calculated spin polarization of the Fe CVV Auger transition as a function both of Auger matrix element (singlet/triplet ratio, proportional to the exchange correlation strength) and of the initial core-hole spin polarization P for a given valence band spin polarization ($P_{VB}=27\%$). Open circle: measured electron-energy-integrated spin polarization of on- L_3 -resonance Fe $L_3M_{45}M_{45}$ Auger spectrum ($P_{on}=37\%$). Filled circle: off- L_3 -resonance value ($P_{off}=20\%$). These measurements carry important information on both the spin polarization of the valence band and the relative strength of exchange correlation, and demonstrate the importance of exchange correlation in itinerant 3d-metals such as Fe. See B. Sinkovic, E. Shekel, and S. L. Hulbert, *Phys. Rev.*, B52, 15703, (1995).

SOFT-X-RAY MAGNETIC CIRCULAR DICHROISM

Transmission measurements from thin evaporated Fe, Co, Ni films were carried out by the NRL group (Y. U. Idzerda, V. Chakarian, and K. Kemner) and the AT&T group (J.-H. Park, G. Meigs, and C. T. Chen) at beamline U4B to determine the absolute photoabsorption cross sections for these important elements. Photoabsorption coefficients of left- and right-circularly polarized soft x-rays were reported, as well as the total photoabsorption coefficients. This group also observed very large magnetic effects in the L-edge extended x-ray absorption fine structure (EXAFS) of 3d transition metals. Transmission MCD measurements extended to the EXAFS region were measured for Fe, Co, and Ni thin films grown under ultra-high vacuum conditions by e-beam evaporation. The EXAFS and magnetic EXAFS (MEXAFS) measurements for the L-edges of 3d transition metals are shown in Figure 7. The topmost panel of Figure 7 shows the Fe XAS spectrum in which the vertical scale in the EXAFS region is expanded. The next panel shows the Fe MCD signal, where the vertical scale has been expanded. Similar measurements at the L-edge of Co and Ni thin films are shown in the remaining panels. Large EXAFS oscillations were observed in the MEXAFS spectra for all three samples. The amplitudes of the oscillations at the L edges are much greater than those observed at the K edges of the same elements. These authors also noted that the relative amplitude of the MEXAFS oscillations compared to the EXAFS oscillations is largest for Fe and smallest for Ni, although the ratio does not scale linearly with the magnitude of the magnetic moment.

Figure 7 U4B: L-edge extended x-ray absorption fine structure (EXAFS) transmission magnetic circular dichroism (MCD) spectra from Fe, Co and Ni thin films electron-beam evaporated onto one-micron-thick parylene substrates. For each material, the upper panel shows the x-ray absorption spectrum and the lower panel shows the MCD signal. The MCD signal is measured by alternating the sample magnetization at each photon energy.

SCIENCE

X-RAY ABSORPTION SPECTROSCOPY

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INTRODUCTION

X-ray Absorption Spectroscopy (XAS) is one of the key research tools available at the NSLS, and the last year was highly productive for the beamlines specializing in this technique. Nine beamlines on the X-Ray Ring and two on the UV Ring now perform absorption spectroscopy on at least a part time basis. They are U1, U16B, X6A and B, X9B, X10C, X11A, X16C, X18B, X19A, X23A2, and X23B. In addition, XAS related experiments are at times carried out on the microscope at X1B, the microprobe on X26A, and on the wiggler beamlines X21 and X25. U4B is used for circular dichroism studies, and several other of the UV lines are occasionally used for NEXAFS studies. This article presents some selected highlights from 1995's research activities at these beamlines.

The extended x-ray absorption fine structure (EXAFS) technique is unique in its ability to determine structural parameters in sample systems which lack long-range order and are hence unsuitable for x-ray or neutron diffraction studies. These include solutions, clusters, amorphous powders, heterogeneous mixtures, and thin films. EXAFS provides coordination numbers and bondlengths about a selected central atom for neighbors within ~ 5 Å distance, and can provide angular orientation information via polarization or multiple scattering effects. X-ray absorption near-edge spectroscopy (XANES) can provide complementary information about elements' oxidation states and geometries. Much of the strength of the technique derives from the fact that samples can be solid, liquid, or even gaseous; at any temperature and any pressure. This versatility has resulted in the application of XAS to a vast range of problems.

One of the most active areas of development within the XAS field is *in situ* experiments, wherein some control or process is exerted on the sample while it is in the x-ray beam. Researchers now employ a myriad of apparatus "on line" to accomplish everything from simply controlling temperature to actually growing samples with molecular beam epitaxy (MBE) chambers. The XAS Workshop of the 1996 NSLS Annual Users Meeting will focus on these kinds of experiments, and presenters will discuss the techniques they have developed.

Figure 1 U4B: Standard EXAFS (above) and Magnetic EXAFS (below) measurements of Fe, Co, and Ni thin films.

RESEARCH HIGHLIGHTS

Magnetism and properties of magnetic materials are a hot research area, and a particular focus of recent work at beamline U4B. The combination of an energy range covering the third row transition metal L-edges and MCD capability enable a wide variety of experiments. Y.U. Idzerda, V. Chakarian, K. Kemner (NRL), J.-H. Park, G. Meigs, and C.T. Chen (AT&T) have made some of the first magnetic EXAFS (MEXAFS) measurements at this facility, studying 3d transition metal films grown on polymer substrates. The magnitudes of the L-edge MEXAFS were found to range from 5% to 0.5% of the corresponding EXAFS signals in Fe, Co, and Ni samples. Sample MEXAFS spectra are shown in Figure 1.

Calcium is ubiquitous in living systems and C.J. Buckley, S.J. Bellamy (KCL), X. Zhang (SUNY@Stony Brook), G. Dermody (KCL), and S.L. Hulbert (BNL) have demonstrated Ca L-edge XANES on beamline U13UA. Five biologically significant calcium salts were measured to assess the possibility of quantifying calcium content and identifying XANES features which correlate with the calcium's chemical environment. Minor peak features in the NEXAFS did show variations with salt composition, opening the possibility of imaging calcium with chemical sensitivity on an x-ray microscope beamline.

The scanning transmission x-ray microscope at beamline X1A is performing such chemically sensitive imaging on a variety of systems. A.P. Smith, H. Ade (NCSU), and E. Rightor (Dow) have studied polyurethane foams, focusing on precipitates which can form in the synthesis of a methylene diphenyl diisocyanate based material. By measuring the carbon k-edge XANES and least-squares simulating the spectra with data from small molecule standards with similar functional groups, as shown in Figure 2, the experimenters were able to determine the compositions of the foam matrix and the precipitates. These were found to differ significantly.

A.P. Smith, H. Ade (NCSU), B. Hsiao, and S. Subramoney (DuPont) used the linear dichroism microscopy capabilities of X1A to study the relative lateral orientation in Kevlar fibers. By measuring the carbon k-edge absorption spectra as a function of polar angle on thin section samples, and least-squares fitting the resulting spectra to determine intensities of the various functional groups, the researchers were able to define a "molecular orientation parameter" which describes the extent to which functional groups are oriented in the fiber. The orientation parameter for the carbonyl functional group, for example, was found to vary systematically with the degree of crystallinity in various Kevlar fiber grades. Planned analogous oxygen XANES measurements are planned to confirm the findings.

Beamline X6A is a dispersive XAS facility, with a

bent crystal polychromator which illuminates the sample with the full bandwidth of energies required for a XAS spectrum at once. A position sensitive detector after the sample records the relative intensities at the various energies. This offers a number of advantages over scanning monochromator beamlines, particularly for time resolved studies and experiments which suffer systematic effects from beam decay. K.J. Gofron, C.W. Kimball (NIU), P.L. Lee, P.A. Montano, and G. Jennings (ANL) studied the temperature dependence of the magnetic x-ray circular dichroism of gadolinium metal at the LIII edge. Below the 290 K transition temperature, Gd is ferromagnetic and the MXCD features, including a quadrupolar peak below the edge, do not vary strongly with temperature. MEXAFS oscillations can be seen at the higher end of the spectra (Figure 3). Above 290 K, in the paramagnetic

Figure 2 X1A: Carbon k-edge absorption spectra of matrix and precipitate areas in polyurethane foam along with decompositions into functional group contributions.

region, the MXCD intensities drop with increasing temperature. However, some features are evident throughout the studied temperature range.

G. Coulston, R. Harlow (DuPont), S.R. Bare (Dow), H. Kung, K. Birkeland, G. Bethke (Northwestern U.), J. Quintan, J. Georgopoulos (DND-CAT), and P.L. Lee (ANL) used the time resolved capabilities of X6A to study a vanadium phosphate catalyst which oxidizes butane to form maleic anhydride. Using a catalyst cell with Be windows and a mass spectrum detector on line, the experimenters were able to record the spectra of the catalyst while monitoring the rate of formation of maleic anhydride. By alternately flowing air and butane into the cell, the rates of both catalyst reduction and reoxidation

could be monitored. The researchers found that the anhydride formation rate correlated with the amount of V^{+5} present, identifying that component as required for catalysis, and that the catalyst reoxidation rate was always slower than the reduction with butane.

L. Chen, M. Wasielewski, W. Svec, K. Huang, and P. Montano (ANL) studied model systems for the chlorophyll dimers important in photosynthesis. The distance between macrocycle planes and their configurations are believed to control their photophysical

properties. Using lab synthesized complexes in which two metal containing chlorophyll macrocycles are linked together via cyclophane linkages, the researchers looked for features in the EXAFS spectra resulting from a metal-metal interaction. Of samples with nickel, copper, and zinc, only the latter showed evidence for a metal-metal interaction: a peak at $3.5 \text{ \AA}$ in the Fourier transform assigned as Zn-Zn (Figure 4). Addition of a coordinating base resulted in attenuation of the peak magnitude, as expected. The nickel bischlorophylls were found to vary between four, five, and six coordinate depending on the presence of coordinating bases and temperature.

Nitrogenase, the protein system responsible for the direct fixing of atmospheric nitrogen by plants, contains a $[4Fe-4S]^{+2}$ cluster. R.C. Scarow, N. Taufen (Haverford College), L.C. Seefeldt, and W.N. Lanzilotta (Utah State University) studied the interaction of nitrogenase iron protein with magnesium ATP to see whether the iron sulfur complex is affected. Previous results from other techniques had been interpreted to suggest that MgATP binding might partially convert the $[4Fe-4S]^{+2}$ cluster into smaller $[2Fe-2S]^{+}$ clusters. In experiments on beamline X9B, the research team found that XANES and full EXAFS spectra on the oxidized iron protein in the presence and absence of MgATP were essentially identical, however. In both cases, each iron was found to have approximately 3 irons and 4 sulfurs as neighbors.

The hydrogenases are among the few metalloproteins which contain the element nickel. Z. Gu, S.B. Choudhury, C.B. Allan, and M.J. Maroney (University of Massachusetts) are working to elucidate

Figure 3 X6A: Magnetic Circular X-ray Dichroism spectra of the gadolinium L_{III} edge as a function of temperature from 94 to 350 K.

the role of the nickel, which appears in an active site together with an iron atom. The team measured the nickel k-edge XAFS spectra of the carbon monoxide adduct of a specific organism's hydrogenase along with the "CO off" form generated via photodissociation. The effects on the spectra are a half eV shift in the edge position and a shortening of the Ni-Fe bond length. The researchers interpret these results to indicate that the CO doesn't bind to the Ni atom, but instead to the Fe site.

S. Bajt (University of Chicago), J.F. Lee (SRRC), S.B. Clark (SREL, University of Georgia), G.M. Lamble (Brookhaven National Laboratory), C.A. Langton and J.

Figure 4 X6B: Fourier-transformed Zn k-edge EXAFS of Zn-bis chlorophyll with and without pyridine in solution at 290 K.

Oji (Westinghouse Savannah River Company) used XANES and EXAFS techniques on beamline X11A to investigate chromium waste as immobilized in cement. Chromium in the +6 oxidation state, as in CrO_4^{2-} , is highly soluble and toxic in comparison to the Cr^{3+} form. Hence, formulations of cements have been developed to favor the reduced form. As evident in Figure 5, simulated waste streams which consist initially of only Cr^{6+} are largely converted to Cr^{3+} in two of the cement mixtures. EXAFS results show that the large bondlength differences between the +6 and +3 forms can be used to help quantitate the relative amount in each state.

D.L. Adler, and R. Nuzzo (University of Illinois) studied bimetallic clusters generated by depositing Re and Ir precursors on an alumina support and then activating with heat under flowing hydrogen gas. EXAFS spectra were recorded on these samples on beamline X16C. The researchers made use of average coordination numbers to estimate cluster size, and the appearance or lack of ordered shells at distances beyond the first shell to infer position relative to the cluster core or periphery. They infer that Ir occupies core sites, while Re appears at the cluster edge.

M.A. Vairavamurthy, S. Wang, B. Khandelwal, and B. Manowitz (DAS, BNL) have been studying sulfur in the environment, particularly in marine sediments. The researchers have previously established that sulfonates are a major class of the organic sulfur in near-surface marine sediments. In order to ascertain whether phytoplankton debris could be the source of this form of sulfur, the investigators measured S k-edge XANES spectra of samples of various types of phytoplankton species on beamline X19A. Sulfonate sulfur was indeed found to be the dominant form in phytoplankton, in support of this idea. The dominance of sulfonates further suggests that they play an as yet unknown, but important role in the cellular biochemistry of marine phytoplankton.

Researchers from the University of Michigan have been studying organocuprate reagents in solution in an effort to understand these potent tools for organic synthesis. In the latest studies, H. Huang and J.E. Penner-Hahn performed Cu k-edge EXAFS measurements on phenylcopper prepared from the addition of phenyllithium to Copper(I)iodide at X19A. The Fourier transform magnitude, shown in Figure 6, shows a very strong peak at just over 2 Å which is consistent with a copper scatterer. A quantitative analysis suggests a Cu-Cu distance of 2.45 Å, which is shorter than the interatomic distance in copper metal, but similar to the distances observed in crystallized pentameric phenyl-copper clusters. Hence, the researchers conclude that similar species are present in solution.

Figure 5 X11A: Chromium k-edge XANES of: (a) a Cr(VI) standard (K_2CrO_4), (b-d) Cr waste in three different concrete mixture immobilizers, and (e) a Cr(III) standard (CrOOH).

EXAFS experiments are optimally combined with other techniques to enhance the information content available at the start of the quantitative analysis. A.C. Carter, M.I. Bell, K.M. Kemner (NRL), C.E. Bouldin,

Figure 6 X19A: Fourier-transformed Cu k-edge EXAFS of phenylcopper in THF solution.

Figure 7 X25: Iron K_{β} emission spectrum of oxidized, high-spin Rubredoxin excited at 7200 eV.

J.C. Woicik (NIST), and S.A. Majetich (CMU) have used a combination of XAS, FTIR, and elemental analyses to determine the structure of cadmium-selenide nanoclusters in work on X23A2. The combination of EXAFS and FTIR was particularly fruitful as it was possible to observe that Se atoms at the surface of the clusters are bare, i.e. bound only to cadmium atoms with a net coordination less than that in the interior of the cluster. The FTIR spectra agreed, with no evidence for Se-ligand modes. Surface cadmium atoms, on the other hand, were confirmed to bind passivating perchlorates.

Zeolites are large, open framework structures made up of tetrahedral silicon and aluminum oxide building blocks. Their pore and cavity structures make them ideal supports as catalysts, and they are employed in a number of industrial processes. M. Endregard (University of Trondheim), A.F. Gualtieri, S. Quartieri, G. Vezzadini (University of Modena), and K.I. Pandya (NCSU) studied the nature of iron found in four naturally occurring zeolites with spectroscopy on beamline X23B. The researchers worked to distinguish whether iron has (1) been substituted for Si or Al into the framework, (2) exists outside the framework, or (3) is associated with hydroxides or other impurities. From Fe k -edge XANES studies, and in particular the relative magnitude of the 3d π peak, it was concluded that the iron has largely octahedral coordination, which is inconsistent with simple substitution

into the framework.

X. Wang, A. Froeschner, and S.P. Cramer (University of California, Davis) have demonstrated the first spin-polarized XANES measurements on a metalloprotein using high-resolution monitoring of the iron K_{β} fluorescence at beamline X25. The Fe K_{β} emission spectrum of oxidized, high-spin Rubredoxin is split into two regions corresponding to decay into a spin-up or spin-down core hole (Figure 7). Thus by monitoring the appropriate fluorescence energy it is possible to separately measure the absorption spectra arising from excitation of the two inner shell electrons. The edges in Figure 8 demonstrate this well: as high spin Fe (III) has five d -shell electrons with the same spin, the quadrupole allowed $1s$ - $3d$ transitions are only available to the core electron with anti-parallel spin. Hence, only one of the absorption spectra shows the familiar 3d π peak.

CONCLUSION

As in past years, the high scientific productivity illustrates that x-ray absorption spectroscopy is in a healthy state at the National Synchrotron Light Source. Good progress has been made in the move towards greater cooperativity between XAS beamlines: the first step of creating a common data collection package to ease user support and training issues has been completed.

Figure 8 X25: Spin-polarized iron k -edge XANES of oxidized, high-spin Rubredoxin illustrating different cross-sections for $1s$ electrons with spin parallel and antiparallel to $3d$ electron spins.

SCIENCE

X-RAY SCATTERING AND CRYSTALLOGRAPHY

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SMALL-MOLECULE SINGLE-CRYSTAL

The use of imaging plate area detectors is extending from the field of protein crystallography into the small-molecule regime. It is permitting the collection of data from samples previously considered too small for conventional point-by-point diffractometry. The use of an integrating area detector greatly reduces the time for data collection and minimizes the influence of instabilities in the beam and the beamline. X3A1 has been the location of a range of experiments by the Stony Brook group led by John Parise involving crystals with sizes in the 20 micron range. For example, K. Tan studied novel open-frame structures in Antimony Sulfide templated by dimethylammonium (prepared by hydrothermal synthesis), and J.-H. Park studied a new compound SrAu_2O_4 prepared by a solid-state reaction of SrO_2 and Au_2O_3 at high pressure and several other compounds (Figure 1). Successful structure determinations were performed in spite of the small size of the crystals involved.

Figure 1 X3A1: Projection of the Structure of SrAu_2O_4 along [100]. The AuO_4 units and Sr ions are represented by the planes and circles.

POWDER DIFFRACTION

Powder diffraction continues to show its effectiveness when even such small single crystal samples are unavailable. A wealth of new structures is reported in the Activity Report, and it is impossible to mention them all here. In an area which is not usually well-represented in SR-based powder work, that of phase identification, is addressed by R.E. Dinnebier and collaborators. They addressed the issue of polymorph impurities in drug compounds. They were able to demonstrate the ability to determine the presence of gamma-phase impurities in alpha-indomethacin, an anti-inflammatory drug, down to levels of at least 0.1% (Figure 2). This limit was imposed by the purity of the reference "pure" material available.

The recent reports of giant magnetoresistance effects in $\text{La}_{(1-x)}\text{Ca}_x\text{MnO}_3$ prompted Radaelli and coworkers to look for structural changes in this region. A rich variety of structural changes was reported around T_c , depending on the value of x .

The ubiquitous imaging-plate finds application in powder-diffraction studies, too. The moving-image-plate setup at X7B has provided a time-resolved capability which has allowed studies of a variety of reactions. An example is the Kolbe-Schmitt reaction for the production of salicylic acid. The reaction mechanism is still poorly understood in spite of its industrial importance. *In situ* diffraction from this system by a collaboration between X7B and X3 (P. Norby, J. Hanson, R.

Figure 2X3B1: Intensity of the (120) reflection of the α -phase of indomethacin for various levels of α contamination.

Figure 3X7B: In-situ X-ray Powder Diffraction diagrams of the carboxylation of sodium phenolate.

Dinnebier, and P. Stephens) has revealed a variety of intermediate phases (Figure 3). The detailed structure of these intermediates is currently being investigated using high-resolution powder diffraction.

The hard x-ray spectrum from the superconducting wiggler which feeds beamline X17 is put to good use by the high-pressure diffraction community. Both X17C and X17B1 hosted a wide range of high-pressure experiments, primarily by the groups from SUNY at Stony Brook (CHiPR), NRL and the Carnegie Institute of Washington. The experiments performed range from studies of minerals under conditions similar to those deep in the earth's mantle, to investigations of the phase diagram of hydrogen at high pressure. An interesting example of the possibilities in a non-geological area is provided by the experiment of E. Skelton and colleagues who were able to study the absorption of deuterium into bulk palladium at high pressure. Although heavily studied, some of its properties at high concentration (~85%) still remain unexplained. The high intensity available at X17C allows data to be collected from volumes as small as 10^{-11} m^3 . They were thus able to study the dynamics of the alpha-beta transition (induced by D absorption/desorption) as a function of depth inside a bulk (1mm thick) sample. They show that whereas the alpha phase forms rapidly at all depths, there is considerable delay in the onset of the beta phase formation at the core of the sample.

SMALL-ANGLE SCATTERING

Bubeck and a collaboration involving Dow Chemical, Cornell and NSLS performed real-time studies of plastic deformation in rubber-modified engineering thermoplastics using the high-intensity wiggler beamline X25. They used a Reticon detector in combination with optical data to collect over 200,000 SAXS patterns with time resolution down to 3ms. They were able to show that previous conclusions regarding the importance of the different possible plastic strain mechanisms

were incorrect, and to allow better engineering of new polymer blends. At beamline X3A2, A.D. Kennedy and a team from DuPont and SUNY Stony Brook has performed experiments using an apparatus which allows tensile deformation experiments without requiring high data rates. Their apparatus used a continuous-feed arrangement wherein a fiber is drawn from a spool over two rollers moving at different speeds (thereby imparting the strain). Since the process is continuous, high quality data can be collected. They were able to collect WAXS data showing a sufficient number of clear reflections to allow crystallographic analysis of the Brill transition, and to confirm that the transition results from anisotropic crystal

thermal expansion (Figure 4). Inter-chain spacing within the H-bonded sheets remains essentially constant while inter-sheet spacing increases sharply, forming a metrically hexagonal structure.

X-RAY HOLOGRAPHY

In an interesting series of experiments at beamline X14A, T. Gog and collaborators have demonstrated a new technique for hard x-ray holography. By measuring the integrated fluorescence intensity as a function of sample orientation, they are able to reconstruct the local environment around a selected atom in a crystal. The technique they use is unusual in that it is the inverse of the more obvious technique of measuring the angular distribution of fluorescent radiation with a stationary sample. In the new scheme, the changes in the elastically-scattered radiation field as a function of sample orientation is used to probe the fluorescent atom position. It is in some sense a generalization of the standing wave technique. Tests of the idea on a Fe_2O_3 crystal and a Ge crystal have demonstrated its potential.

STANDING-WAVES

The standing-wave method is not limited to crystalline substrates. Bedzyk and co-workers at X15A have performed some measurements in the total external reflection regime to investigate the adsorption of a thin film of copper on a polymer layer on a polished substrate. Such configurations are of growing interest to a variety of technologies. The variations in the standing-wave pattern near the substrate critical angle can give information on the location and thickness of the film following thermal treatment. The copper was seen to form relatively thick islands as deposited, and following annealing to become thinner. No interdiffusion of the copper into the polymer beyond 5 Å was observed. One of the problems with the standing-wave method is the need for the adsorbate atom to provide a signal in response to excitation by the standing wave field strength. This has traditionally been x-ray fluorescence from a high-Z adsorbate. Many systems of interest involve low-Z adsorbates, making this technique inappropriate. Berman, Heskett and Kao have shown that photoemission can equally well be used as this signal mechanism, and they studied half-monolayer coverages of CO on nickel (111) surfaces. They were able, using a cylindrical-mirror electron energy analyzer, to separately record signals from carbon, oxygen and nickel core levels (Figure 5). Their results are consistent with those of recent SEXAFS and PED measurements, but not with earlier IR and EELS experiments.

Figure 4a X3A2: Cylindrical co-ordinates for BO2-F18: Calculated model (solid vs data (dashed)).

Figure 4b X3A2: Crystallinity index vs temperature.

Figure 5a X25: Electron energy distribution curve of CO/Ni(111) measured at a photon energy of 3.055 keV.

Figure 5b X25: Measured XSW yields of the Ni $2p_{3/2}$, O 1s, and C 1s core levels as the bulk Ni(111) Bragg reflection (at bottom) was scanned, compared with theoretical fits, for c(4x2) CO/Ni(111).

MAGNETIC SCATTERING

The first observation of surface magnetic scattering has been performed by G. Watson and collaborators taking advantage of the large resonant enhancements accessible near the Uranium M_{IV} edge. In experiments at beamlines X22C and X25 they were able to measure the dependance of the magnetic scattering truncation rod as a function of momentum transfer, photon energy and temperature, which gives information about the magnetic

order in the surface and near surface region of the sample. They have been able to model all this data, and have shown that the magnetic phase transition is continuous at the surface. This is not so surprising, but they also demonstrated that the sub-surface region also does not show first-order behaviour, in contrast to similar non-magnetic surface-scattering results from other systems. The addition of a high-field superconducting magnet to the X22B spectrometer has enabled a series of magnetic scattering experiments on low-moment systems. An example of this is the work of V. Kiryukhin and collaborators to elucidate the magnetic phase diagram of the spin-Peierls system CuGeO_3 (Figure 6). This material is a one-dimensional antiferromagnet. At low temperatures the lattice dimerizes to lower the magnetic ground-state energy. The Zeeman energy corresponding to a 12T applied field lowers the energy of the first excited state enough to induce a transition into an incommensurate spin-lattice modulated phase. This phase had previously been inaccessible to scattering probes. These measurements have shown that this phase is a soliton lattice, and have given the inter-soliton distance and soliton width as a function of applied field and temperature. The measured soliton width is almost double that predicted theoretically, providing a challenge for the theory of one-dimensional quantum magnetism.

Figure 6 X22B: Scans through the (3.5, 1, 2.5) superlattice reflection of CuGeO_3 at $T=4\text{K}$ in the Incommensurate phase. Successive scans were multiplied by 100 in order to achieve a constant offset on the logarithmic scale. The lines are the results of fits to resolution-limited Gaussians.

DIFFUSE SCATTERING

The study of x-ray diffuse scattering can provide information about disorder, both static and dynamic, in crystalline materials. Gibaud and collaborators have used the high-energy radiation available at beamline X17B1 to advantage in such work. They point out that the Ewald sphere is so large at, say, 60keV it is essentially flat over the plane of the recording medium (in this case an imaging plate). This greatly simplifies the interpretation of such data, since only one scattering plane is imaged at a time, and the lines of constant indices are nearly straight. They illustrated these points with a series of measurements on a 3mm thick sample of KMnF_3 (Figure 7). They were able, for the first time, to image the entire RM branch of the Brillouin zone through two phase transitions, one at 186K and a second at 100K. The R point condenses at 186K, but there is still intensity in the RM line until it disappears at 100K, as the M point condenses.

INELASTIC SCATTERING

It has long been held that a high-resolution study of the Compton scattering in the region where the core and valence contributions cross over would reveal a discontinuous change. This "Compton step" has never been observed experimentally. It has been assumed that this failure was a resolution problem. K. Hämäläinen, using the high-resolution inelastic scattering instrument at X21, has shown that the step is smeared out on a scale well above the resolution limit of that instrument. There is currently no theoretical model which can explain this smearing. The high-resolution fluorescence spectroscopic techniques developed at NSLS were put to an interesting use by W. Caliebe *et al.* at beamline X25. They used the spin-dependence of the fluorescence satellites to perform spin-dependent resonant Raman scattering studies of Gd at the L_{III} edge. The use of a quarter-wave plate to generate circularly-polarized x-rays allows the selective excitation of spin-up or spin-down electrons in a magnetically aligned sample. The spin-orbit splitting is clearly observed in the dipole-allowed transition $2p^{54f^{n+1}5d^0} \rightarrow 3d^{94f^{n+1}5d^0}$.

LIQUIDS

Scattering from liquid surfaces received significant attention this year. Two liquid surface scattering stations were in operation, one at X22B and another at X19C. In addition the X22B setup was used at X25. Regan *et al.* at X25 studied surface ordering in pure Hg and Ga. They observed differing behaviour in these two elements. In

(a) The [010] direction is vertical and the [100] direction is horizontal.

(b) The [010] direction is vertical and the [101] direction is horizontal.

(c) The [010] direction is vertical and the [301] direction is horizontal.

Figure 7 X17B1: High energy x-ray monolayer patterns of the (001), (101) and (103) scattering planes.

Hg they observed evidence of surface ordering, with the ordered layer thickness similar to the bulk pair correlation length. In Ga this ordered layer appears to extend deeper into the bulk liquid.

Ning Lei and colleagues at X19C studied surface segregation of Bi in Bi-doped Ga. They found that the reflectivity of the liquid surface could be well described by a model in which a complete Bi layer sits on top of bulk liquid Ga (Figure 8). They are currently extending this work to include Ga:Sn alloys.

Metals were not the only liquids to be studied. The liquid-liquid interface in a ternary system of water, decane and C4E1 (an oil) were studied at X19C by Williams and co-workers. These systems exhibit ultra-low surface tensions and the interfaces are expected to have large-amplitude thermal fluctuations. The data suggests an interfacial roughness of order 50 Å compared to the molecular size of 9 Å. This difference is attributed to the enhanced thermal fluctuations. Deutsch and collaborators continued their studies of surface freezing in alkanes at X22B, moving towards an understanding of surface ordering in liquid binary alkane mixtures. These mixtures introduce an extra degree of freedom compared to pure alkane samples which may lead to prewetting, surface enrichment and surface layering. For large differences in alkane molecular weights, discontinuous changes were observed involving surface segregation and several 2-D structural phase transitions. Theoretical models are being developed to explain these observations.

NUCLEAR RESONANT SCATTERING

The properties of near-monolayers of rare gases adsorbed on graphite have been, and continue to be, the subject of much study for many years. Almost all of the previous work has concentrated on the static structure of such films using diffraction of x-rays or neutrons. Even so there is still controversy surrounding the details of the rich phase diagrams which have been uncovered. Nuclear resonant scattering offers the possibility of studying in detail the dynamics of these phases. D. Johnson performed such a study on beamline X12A. ^{83}Kr has a convenient nuclear resonance at 9keV, and he was able to produce an optical system suitable for measuring the nuclear forward-scattering which contains the dynamic information. He discovered that there is significant lattice softening near a commensurate-incommensurate phase transition boundary, followed by a significant stiffening of the layer as it approaches completion.

Figure 8 X19C: (left) circles denote the experimentally obtained specular reflection after divided by the theoretical Fresnel reflectivity for gallium. The solid line denotes the fit to a complete bismuth monolayer on top of bulk of liquid gallium. (Right) The atomic distribution to the interface, obtained from the fit.

SCIENCE

X-RAY TOPOGRAPHY

Michael Dudley
SUNY at Stony Brook

This report outlines some of the significant results obtained from the two beamlines mainly comprising the NSLS X-ray Topography Special Interest Group: X19C and X23A3.

A broad range of experiments has been carried out on X19C in the last year. The following are selected highlights. In a project funded by Cree Research Inc. via ARPA/AFOSR, C. Carter, V. Tsvetkov and R. Glass of Cree Research Inc., and W. Si and M. Dudley of Stony Brook carried out a detailed study of micropipes (hollow core screw dislocations) in 6H-SiC single crystals grown at Cree Research Inc. using Physical Vapor Transport method. The Burgers vector of the micropipes, b , was determined using two relative and two absolute techniques via Synchrotron White Beam X-ray Topography, with good agreement being obtained for four sets of data. One of the absolute techniques involves the measurement of the lattice tilt either side of the dislocation core by recording transmission projection white beam images at different specimen-film distances and measuring the tilt angle between the two components of the bimodal images which are longitudinally shifted with respect to each other. An example showing the mutual shift of the bimodal dislocation image components recorded at two specimen-to-film distances is shown in Figure 1. From the lattice tilt S and image width W , both the sense and magnitude of Burgers vector could be determined. The other absolute technique involves explicitly mapping the lattice tilt around the micropipe from topographs recorded in the transmission section geometry as shown in Figure 2. The diameters of corresponding hollow-cores of the dislocations (i.e. the diameters of the micropipes), D , were measured using Scanning Electron Microscopy. The relationship between micropipe Burgers vector magnitude and diameter, $D = \mu b^2 / 4\pi^2 \gamma$, (μ is shear modulus, γ is specific surface energy), as predicted by Frank [F. C. Frank, *Acta Cryst.*, 4, 497-501, (1951)], was then tested. Good agreement was found, as shown in Figure 3.

Figure 1 X19C: Projection transmission x-ray topographs showing a screw dislocation (micropipe) image M, in 6H-SiC, $g = 0006$, $\lambda = 0.89 \text{ \AA}$, recorded at two specimen-to-film distances Dsf. S is the lattice tilt, W is the image width. (a) Dsf = 5 cm, and (b) Dsf = 17 cm. Research supported by ARPA/AFWL under Grant No. FY33615-95-C-5426 through Cree Research, Inc. under Grant No. 95-004.

Figure 2 X19C: A section transmission x-ray topograph showing a screw dislocation (micropipe) image M, in 6H-SiC, $g=0006$, $\lambda=0.89$ Å, recorded at specimen-to-film distance $D_{sf}=16$ cm. Research supported by ARPA/AFWL under Grant No. FY33615-95-C-5426 through Cree Research, Inc. under Grant No. 95-004.

Figure 3 X19C: Relationship between the magnitude of Burgers vector of screw dislocation, b , and the diameter of the associated micropipe, D . Research supported by ARPA/AFWL under Grant No. FY33615-95-C-5426 through Cree Research, Inc. under Grant No. 95-004.

Figure 4 X19C: Synchrotron white beam X-ray topograph ($g=440$, $\lambda=0.64\text{ \AA}$) recorded in reflection geometry from a (110) InP wafer cut from a MLEK grown [001] boule showing slip bands (SB) originating from the shoulder region of the boule. Research carried out under the auspices of ARPA/AFOSR Consortium for crystal growth research (Contract No. F496209510407).

Figure 5 X19C: Synchrotron white beam X-ray topograph ($g=400$, $\lambda=0.52\text{ \AA}$) recorded in transmission geometry from a (001) InP wafer cut from a LEK grown [001] boule showing a well defined four-fold symmetric distribution of dislocations. Research carried out under the auspices of the Stony Brook ARPA/AFOSR consortium for crystal growth research (Contract No. F496209510407).

In work carried out under the auspices of an ARPA/AFOSR funded consortium studying the growth of InP and other semiconductor crystals, V. Prasad, H. Zhang, W. Si, H. Chung, and M. Dudley of Stony Brook, and D. Bliss and A. Anselmo of Rome Airforce Laboratories have been correlating defect microstructures and interface shapes observed using Synchrotron White Beam X-ray Topography (SWBXT) with the theoretical predictions of heat transfer and stress generation during the single step, high pressure Kyropoulos growth of doped InP boules. Figure 4 shows a reflection topograph recorded from a wafer sliced longitudinally from an [001] boule. Stress concentration, leading to slip band generation, is clearly observed at the neck region of the boule. This correlates well with stress calculations. Figure 5 shows the distribution of

dislocations in a typical 001 wafer cut from a [001] boule. Note the four-fold symmetry of the dislocations' distribution. This four-fold symmetry is predicted from resolved shear stress calculations, as shown in Figure 6. Interface shape is often revealed on x-ray topographs due to the periodic variation on dopant concentration as the interface migrates during growth. Control of the shape of the interface is crucial to minimize defect generation and propagation, and its observation is a primary indicator of the degree of thermal control during the growth process. Figure 7 shows an example of an observable interface. The observed shape agrees well with theoretical predictions pertinent to the particular growth chamber used [H. Chung, W. Si, V. Prasad, H. Zhang, and M. Dudley, to be published].

Figure 6 X19C: Distribution of resolved shear stress in [001] LEK grown InP crystals subject to thermal-gradient-induced, uniformly distributed, radially compressive, hoop stresses. Stress calculations revealed that maximum stresses were concentrated in the $\langle 100 \rangle$ directions while minimum stresses were induced in the $\langle 110 \rangle$ directions. The calculated results are consistent with our experimental observations. Research carried out under the auspices of the Stony Brook ARPA/AFOSR consortium for crystal growth research (Contract No. F496209510407).

In a project funded by the Army Research Office and NSF I. Baker, X. Hu of Dartmouth College, and M. Dudley of Stony Brook have carried out detailed in situ straining studies of notched ice single crystals., in order to examine the generation and multiplication of dislocations in the vicinity of notches, and in particular to determine if a dislocation-free zone exists as previous etch pit investigations by other workers seemed to indicate. Results obtained from single crystals of three different orientations, numbered 1 to 3, as shown in Figures 8, 9, and 10, indicate that the deformation is dominated by basal plane dislocations, and that no dislocation free zone exists.

Figure 7 X19C: Synchrotron White Beam X-ray Topograph ($g=00\bar{4}$, $=0.45\text{\AA}$) recorded from a longitudinal cut (110) S doped In P wafer showing the morphology of the growth interface (I) and the formation of slip bands (S_1 to S_3). Research carried out under the auspices of ARPA/AFOSR Consortium of crystal growth research (Contract No. F496209510407).

Figure 8 X19C: Dislocation motion at notch tips in ice single crystals: (a) crystal and notch orientations for specimen 1. (b) Dislocation structure prior to loading. The (0001) planes are normal to loading direction and are, thus, horizontal and seen edge-on. (c) Image (load removed) taken after application of a stress of 0.22 MPa for 45 minutes and 0.44 MPa for 20 minutes at -13°C . Note that the dislocations have increased their lengths due to glide on the basal planes. $g=10\bar{1}0$ in both b and c. Research funded by the Army Research Office through Grants No. DAA-L03-92-G-0319 and No. DAA-H04-93-G-0061 and in part by the donors of the Petroleum Research Fund which is administered by the American Chemical Society.

Figure 9 X19C: Dislocation motion at notch tips in ice single crystals: (a) Crystal and notch orientations of specimen 2. (b) Topograph ($g=10\bar{1}0$, load on) taken after application of a stress of 0.22 MPa for 10 minutes at -13°C . Note dislocation bundles which run in the Burgers' vectors directions $[11\bar{2}0]$ and $[2\bar{1}\bar{1}0]$. Research funded by the Army Research Office through Grants No. DAA-L03-92-G-0319 and No. DAA-H04-93-G-0061 and in part by the donors of the Petroleum Research Fund, which is administered by the American Chemical Society.

Figure 10 X19C: Dislocation motion at notch tips in ice single crystals: (a) Orientation of specimen 3 (b) Prior to loading (c) 0. 15 MPa for 13 min. 0.31 MPa for 4 min., and 0.45 MPa for 7 min., at -15°C. Research funded by the Army Research Office through Grants No. DAA-L03-92-G-0319 and No. DAA-H04-93-G-0061 and in part by the donors of the Petroleum Research Fund, which is administered by the American Chemical Society.

Figure 11 X23A3: A (111) asymmetric transmission image showing a stacking fault (S) in the substrate and a linear array of dislocations. (D) in the CVD film.

Continuing their investigation of defects in CVD diamond, David R. Black and Harold B. Burdette from NIST and Mary Anne Plano, M. Dale Moyer and Miguel A. Moreno from Crystallume have observed individual defects in a homoepitaxial CVD diamond film. A high-quality, low-stress 200 μm thick epitaxial diamond film was grown on a 400 μm thick high-temperature/high-pressure type IIa diamond. A direct correlation was found between defects in the film and substrate defects as shown in Figure 11. The area of the film with the lowest defect density was grown on a nearly defect-free part of the substrate. Within this region, individual defects are seen in the film. Stacking faults in the substrate, which terminate at the deposition surface, appear to result in linear arrays of dislocations in the film. These linear arrays are the same length as the termination line of the stacking fault and are comprised of individual dislocations, in regions where dislocations in the substrate terminated at the surface, more strain was observed in the film.

Beamline X26A: Synchrotron x-ray fluorescence false color contour maps of major element concentrations (FeO and MnO), and of a trace element concentration (Y) for an almandine garnet from Connecticut, USA. Yellow color represents the highest concentration on these scans and the whole width of these scans is 4.25 mm. At lower left is a photomicrograph of this mineral. [A. Lanzirotti, State University of New York @ Stony Brook]

THREE MEETINGS & WORKSHOPS

MEETINGS

THE 1995 NSLS ANNUAL USERS' MEETING

Paul Zschack

ORNL / Oak Ridge Institute for Science and Education

NSLS Users' Executive Committee Chairman

The NSLS held its 14th Annual Users' Meeting May 9-10, 1995 at Brookhaven National Laboratory. Associated with the 1995 Meeting, 5 parallel workshops were held on May 8th, and a satellite workshop on XAFS was well attended on May 7th. The workshop and scientific programs emphasized scientific productivity and recognition of the NSLS as a mature user facility.

William Oosterhuis from the U.S. DOE next offered cautiously encouraging words regarding the outlook for future funding, and was particularly optimistic about the favorable reception which the "Facilities Initiative" has received.

NSLS Acting Chairman Denis McWhan gave a report on the state of the facility. Even though the next

(left to right): Cullie Sparks (Oak Ridge National Laboratory), Denis McWhan (Associate Director Basic Energy Science Programs, BNL and Chairman, National Synchrotron Light Source), and Tony Cheetham (University of California @ Santa Barbara).

Keynote Speaker, Robert Galvin, Chairman of the Executive Board of Motorola, Inc. and Chairman of the Secretary of Energy Advisory Board Task Force on Alternative Futures for the DOE National Laboratories.

Following opening remarks by BNL Deputy Lab Director Marty Blume, Cullie Sparks (ORNL) gave the inaugural NSLS Distinguished User Presentation. This was a thoroughly enjoyable retrospective talk that served to remind all users that the reliable operations we currently enjoy did not come easily. Through a series of anecdotes, the efforts of many individuals were acknowledged as important for the evolution of the NSLS as a user-friendly facility.

generation synchrotron sources are coming on line, the NSLS continues to be a vibrant, growing facility with planning for a Phase 3 upgrade and creation of PRT confederations. New beamline commissioning and PRT reorganizations indicate that the NSLS is continually adapting to accommodate the changing needs of the user community.

The morning session ended with the Keynote Address, given by Robert Galvin, Chairman of the Executive

Board of Motorola Inc., and Chairman of the Secretary of Energy Advisory Board Task Force on Alternative Futures for the DOE National Laboratories. Mr. Galvin provided timely insight on the role of Government in the creative process, and most eloquently described his vision for the eventual privatization of the National Laboratories. This is one step beyond the Task Force recommendation for corporatization of the National Laboratory facilities, and introduced users to provocative, challenging new concepts in scientific organization and administration.

The traditional barbecue lunch provided the venue for Special Interest Group (SPIG) meetings and the User Executive Committee elections. Elected to serve 2 year terms were Doon Gibbs (BNL - Physics), Peter Stephens (SUNY @ Stony Brook) and Kim Mohanty (EXXON). In addition, recognizing a significantly growing research area, the User Association voted to create another special interest group for biology.

After lunch, the scientific program began with Joel Berendzen (LANL) showing a wonderfully produced

device concepts. Sam Krinsky (NSLS) detailed the commissioning of the Elliptical Polarized Wiggler, and operations to 100 Hz with no significant adverse impact on operations. With the exciting prospects of easily using circularly polarized light, the EPW holds great promise. Similarly, Peter Stefan (NSLS) discussed the exceptional performance of the Prototype Small Gap Undulator, and noted only minimal compromise on lifetime. The conference poster session, with 80 contributions, was held Tuesday afternoon concurrent with a cocktail reception. The wide diversity of contributions again documents the importance of research done at the NSLS in many scientific disciplines. This year, the conference banquet was held at the Port Jefferson Country Club where the wonderful view and exceptional food were enjoyed by all. In a short after-dinner presentation, the Users' Association and the NSLS staff acknowledged the 5 years of leadership Denis McWhan has given as Chairman of the NSLS.

The meeting resumed Wednesday morning when Eric Isaacs (AT&T Bell Labs) demonstrated use of inelas-

(left to right): Martin Blume (Deputy Director, Brookhaven National Laboratory) and Louis Terminello (Lawrence Livermore National Laboratory, Chairman of SSRL Users' Executive Committee).

(left to right): Xiaodong Zhang and Janos Kirz (SUNY @ Stony Brook), with Christopher Buckley (King's College London).

video demonstration of the crystallography of carbonmonoxy myoglobin. Steve Dierker (U. of Michigan) next provided exciting new results using coherent radiation to study complex fluids. Certainly, protein crystallography and speckle techniques will continue to be important programs at the NSLS and at other synchrotron facilities.

The NSLS continues to work toward improved performance, as evident from the work on new insertion

tic x-ray scattering in probing electronic structure in condensed matter systems. Unlike electron probes, x-rays provide good access to momentum transfer, and give a more complete picture of the dynamic structure factor. Myron Salamon (U. Of Illinois) next explained x-ray resonant magnetic scattering measurements used to detect the induced spin structure in a Dy-Lu alloy film. The growth during the last several years in magnetic scattering studies using x-rays is remarkable. In another important

area, Geraldine Lamble (NSLS) presented several examples of applications of XAFS techniques to study environmental problems.

The next two talks demonstrated continued success on the UV floor. First, John Gland (U. of Michigan) talked about the kinetics of organic reactions on metal surfaces using fluorescence yield measurements with ultra-soft x-rays. The morning session concluded when Eric Jensen (Brandeis U.) discussed advances in high-resolution photoemission techniques. Milli-electron volt resolution photoemission will become even more widely utilized in the next few years.

The lunch break on the second day was an opportunity to acknowledge the Structural Biology building addition to the NSLS. Roland Hirsch from the DOE Office of Health & Environmental Research was joined by BNL Laboratory Director Nicholas Samios, Denis McWhan and BNL Biology Department Chairman William Studier for a ceremonial ribbon cutting. The dedication ceremonies, held indoors at Berkner Hall due to poor weather conditions, were attended by over 300 meeting registrants and NSLS staff which indicates the importance of structural biology programs in the future.

The final session began with Mike Toney (IBM Almaden) presenting an interesting talk on near surface structures in rubbed polymer films. Although there is technological relevance (for example, to flat panel displays), there is also fundamental interest in this behavior. Brenda Laster (BNL - Medical) presented an application of synchrotron radiation to cancer radiotherapy using an enhancement due to Auger electrons, and its potential for diagnostic imaging of malignant breast disease. Her enthusiasm for this work underscores the potential impact

Attendees of the 1995 Annual Users' Meeting examining the display of one of the 24 exhibitors.

of such medical applications. Finally, Mike Regan (Harvard U.) concluded the scientific program with a discussion of reflectivity measurements to understand the surface and near-surface layering structure of liquid metals.

The business of the Meeting was concluded when the UEC, in executive session, selected Peter Stephens (SUNY) the UEC Chair-Elect and Chair of the Organizing Committee for the 1996 Annual Users' Meeting. Planning for the next meeting is already underway.

MEETINGS

17TH INTERNATIONAL FREE

ELECTRON LASER CONFERENCE

Ilan Ben-Zvi and Samuel Krinsky

NSLS

Conference Chairmen

The National Synchrotron Light Source has been pursuing the development of new radiation sources for a number of years. Groundbreaking theoretical and experimental work at BNL, and the NSLS in particular, has strongly contributed to the belief that the next generation of light sources will be Free-Electron Lasers (FELs). In 1992 the Executive Committee of the International FEL Conference decided that BNL would host the 1995 FEL Conference. This decision was a recognition of the work done at BNL on this subject.

The 17th International Free Electron Laser Conference and 2nd International FEL Users Workshop were held August 21-25 in New York City at the Marriott Marquis hotel on Times Square. The FEL Conference was co-chaired by Ilan Ben-Zvi and Samuel Krinsky and the Users Workshop was co-chaired by Erik Johnson and Glenn Edwards of Vanderbilt University. The 267 attendees from 15 countries met to discuss the advances in FEL technology taking place during the last year throughout the world, and to consider the maturing scientific programs at Infrared FEL User Facilities. The FEL Conference and FEL Users Workshop were held in parallel sessions to allow a good interaction between the radiation source scientists and the radiation users. Over 300 papers were presented at the conference. The proceedings, to be published by North Holland, will include about 200 manuscripts in 600 pages of Nuclear Instruments and Methods.

Among the subjects at the center stage of the conference were the development of short wavelength FEL and also high power devices at longer wavelengths.

The participants of the conference enjoyed the outstanding facilities and rooms of the Marriott Marquis hotel as well as the opportunity to visit the Big Apple. Tickets to Broadway shows and City tours that were provided by the conference organizing committee were in great demand. The conference included two receptions (one each for the conference and workshop) and a banquet. Among the events at the banquet was the traditional award ceremony of the FEL Prize and a chamber music concert.

Ilan Ben-Zvi (far left) and conference attendees at Accelerator Test Facility (ATF) Beamline #2 which is the site of the inverse FEL experiment. The tour of the ATF was part of the Wednesday visit to BNL.

Beamline U13UA: View looking into the Extreme Ultraviolet Lithography (EUVL) camera operated by AT&T Bell Laboratories of Lucent Technologies. The mask is on the block on the left, and the wafer is on the right. The 1X Offner camera is suspended overhead; it was assembled and in an initial commissioning phase during FY 1995 and will be capable of exposing wafers over a large (several square millimeter) area. Two low-energy (20-120 eV) Zeiss gratings (160 degrees included angle) were also commissioned, and a resolving power of 5000 was demonstrated at 63 eV photon energy.

FOLIO OPERATIONS

OPERATIONS

VUV MACHINE

Stephen Kramer
VUV Ring Manager

Stephen Kramer, VUV Ring Manager

Figure 1 shows the breakdown of the VUV Ring operating time for the Fiscal Year 1995. The monthly breakdown of these statistics is shown Figures (2 to 6). After a steady improvement in the reliability of operation over the past several years, the unscheduled downtime increased from under 2% to over 3%. This was largely the result of problems with the injection system arising from troubles with the new booster dipole power supply. This will be repaired in FY 1996 and the old power supply will remain available as a hot spare, reducing the likelihood of this situation causing a continued reduction of the beam reliability. Despite this trouble, the integrated current

has increased over FY 1994 level, due to an increase in the number of hours of operation. This increase resulted mainly from a decrease in maintenance and studies time.

The major improvement in the VUV Ring operation has been an increase in the operating energy of the electron beam to 800 MeV. The actual increase in energy from field measurements in the dipole magnets was 8.6% or an increase from 744 to 808 MeV. This increase was confirmed by measurements of the undulator photon energy spectra. The advantage of this higher energy has been a reduction in Touschek scattering rate and an increase in beam lifetime by more than 40% (see Figure 7). This continues the steady increase in lifetime over the last four years, when the 4th harmonic RF cavity was commissioned and used to increase the electron bunch length. Figure 8 shows the improvement in the current per fill resulting from this improvement program. At the operating energy of 800 MeV, a typical 5 hour operational fill decays from 850mA to about 325 mA, almost a factor of two above the current level in 1992. The only negative side of this increase in energy has

been the need to ramp the energy down to the 744 MeV injection level and back up again. This takes less than half a minute to ramp the energy, contributing very little impact on the hours of operation lost due to injection. However, after ramping to 800MeV, the dipole field undergoes a 15-20 minute relaxation to reach equilibrium at the higher field, due to thermal expansion from the higher current in the magnet coils. Since the field change occurs while the user photon optics are warming up and as a result of the Global Orbit Feedback System (GOFBS) holding the beam stable, the users have yet to see any real impact from ramping the ring energy. It is planned that

the booster peak energy will eventually be increased to match the VUV operating energy. Continuing this very successful increase in ring energy and lifetime will remain a high priority for the VUV Ring, however this will not be done if the increase could risk the high reliability of operation that has been achieved. It should be noted that even at the energy level of 800 MeV, this represents a 14% increase in energy from the design value of 700 MeV and a 70% increase in synchrotron radiation power.

The stability of the electron beam orbit was improved this year by the implementation of an RF Frequency Feedback System (RFFFS). This was done by programming a workstation rather than a micro-computer and it corrects the orbit every several seconds by adjusting the RF frequency a few Hertz out of 52.886 MHz. This corrects the horizontal orbit motion by shifting the average beam energy (total energy change

$$\Delta \frac{E}{E} < 2 \times 10^{-5} \text{ or less than 5\% of the natural energy spread}$$

of the beam) as the current and synchrotron power decay, a correction not possible with the present GOFS. The RFFFS has reduced the horizontal rms orbit motion by a factor three and the rms orbit motion at certain position monitors by a factor of 10 to 15. The system as expected has little improvement or adverse effect on the vertical orbit stability. Another improvement in operations has been the commissioning of a real-time tuning of the undulator gaps (U5U and U13U) during user operations. Although this is quite common in higher energy rings (e.g. X-Ray Ring), the lower energy of the VUV Ring makes orbit steering and betatron tune shifts have a greater impact on the bending magnet beamline users. The GOFS has always maintained a stable orbit during these changes, but the tune changes caused flux changes in the high resolution beamlines due to changes in the vertical beam size. A program was written to run on the workstations to compensate for the tune changes using the neighboring quadrupoles, while the gap is being changed. This has shown to be satisfactory for all affected beamlines and is now in routine operation.

Figure 1: The breakdown of the VUV Ring usage based on total time (not scheduled time) for FY95.

VUV Ring Performance FY 1995

Figure 2: The VUV Ring injection charge rate averaged over all fills in each month.

Figure 3: The total integrated current for the VUV Ring accumulated each month.

Figure 4: The injection current averaged over all fills in a month for the VUV Ring.

Figure 5: The VUV Ring vacuum pressure at 500 mA beam current averaged over each month.

Figure 6: The VUV Ring exponential beam lifetime at 500 mA beam current (seven bunch operation only) averaged over each month.

A major new system was added to the VUV Ring during FY 1995, a Superconducting Magnetic Energy Storage device (SMES). This device was provided at no cost to the NSLS and can provide power to maintain the VUV Ring beam during transient loss of AC power for periods of up to five seconds. Although this system has switched-in many times while maintaining the beam in the ring, it has yet to prove itself as a solution to the power transient problem from an operational downtime point of view. Continued study may eventually prove the SMES technology as just such a solution, but in the meantime its cost and impact has not had a negative effect on operations.

Finally, a test of the Top-Off Method of Injecting (TOMI) of the VUV Ring was performed in February. Figure 9 shows the current versus time for this study shift. The beam current was maintained by the injection system at 500 ± 25 mA over a 5 hour shift, by injecting 50 mA approximately every 18 minutes. With the average injection rate of the injection system this could be done in 30 seconds or less, but typically was less than one minute. Measurements of beam orbit stability during TOMI showed factors of 4 to 8 reduction in the vertical and horizontal rms beam motion, respectively. This allowed high resolution ($< 0.1\%$) IR scans to be made over periods of greater than an hour compared to 20 minutes during normal operations. The clear advantage to the users, besides orbit stability, will be reduced power loading effects on their photon beam optics. In order for TOMI

to become an operational reality, considerable effort will be in the areas of radiation safety, injection efficiency and reproducibility, and to reduce the injection transient beam motion (period less than 30 msec. out of the 1.2 second injection pulse period). In fact TOMI has been the injection method of the VUV Ring for years (prior to 800 MeV operations), but with a large dynamic range of current (850 to 250 mA). Once the technical problems are solved, allowing the shutters to remain open during the injections, the users could benefit from more stable beam and flux with the possibility to increase beam brightness without the concern of reduced lifetime that has plagued the VUV Ring operations since its inception.

VUV STORAGE RING PARAMETERS AS OF NOVEMBER 1995

Normal Operating Energy	0.808 GeV
Peak Operating Current (multibunch ops.)	0.85 amp ($0.9 \times 10^{12} e^-$)
Circumference	51.0 meters
Number of Beam Ports on Dipoles	17
Number of Insertion Devices	2
Maximum Length of Insertion Devices	~ 2.5 meters
$\lambda_c(E_0)$	19.9 Å (622 eV)
$B(\rho)$	1.39 Tesla (1.91 meters)
Electron Orbital Period	170.2 nanoseconds
Damping Times	$\tau_x = \tau_y = 13$ msec; $\tau_z = 7$ msec
Lifetime @ 200 mA with 52 MHz	360 min
(with 211 MHz Bunch Lengthening)	(590 min)
Lattice Structure (Chasman-Green)	Separated Function, Quad, Doublets
Number of Superperiods	4
Magnet Complement	<div style="display: flex; align-items: center;"> <div style="font-size: 3em; margin-right: 10px;">{</div> <div> 8 Bending (1.5 meters each) 24 Quadrupole (0.3 meters each) 12 Sextupole (0.2 meters each) </div> </div>
Nominal Tunes (ν_x, ν_y)	3.14, 1.24
Momentum Compaction	0.0235
RF Frequency	52.887 MHz
Radiated Power	20.4 kW/amp of Beam
RF Peak Voltage with 52 MHz (with 211 MHz)	80 kV (20 kV)
Design RF Power with 52 MHz (with 211 MHz)	50 kW (10 kW)
Synchrotron Tune (ν_s)	0.0018
Natural Energy Spread (σ_e/E)	5.0×10^{-4} , $I_b < 20$ mA
Bunch Length (2σ)	9.7 cm ($I_b < 20$ mA)
($2l_{rms}$ with 211 MHz Bunch Lengthening)	(28)
Number of RF Buckets	9
Typical Bunch Mode	7
Horizontal Damped Emittance (ϵ_x)	1.62×10^{-7} meter-radian
Vertical Damped Emittance (ϵ_y)	$\geq 3.5 \times 10^{-10}$ meter-radian (2.8×10^{-9} in normal ops.) *
Power per Horizontal milliradian (1A)	3.2 Watts

Arc Source Parameters

Betatron Function (β_x, β_y)	1.18 to 2.25 m, 10.26 to 14.21 m
Dispersion Function (η_x, η_y)	0.500 to 0.062 m, 0.743 to 0.093 m
$\alpha_{xy} = -\beta'_{xy}/2$	-0.046 to 1.087, 3.18 to -0.96
$\gamma_{xy} = (1 + \alpha_{xy}^2)/\beta_{xy}$	0.738 to 0.970 m ⁻¹ , 1.083 to 0.135 m ⁻¹
Source Size (σ_x, σ_y)	536 to 568 μ m, >60 to >70 μ m (170-200 μ m in normal ops.) *
Source Divergence (σ_x', σ_y')	686 to 373 μ rad, 19.5 to 6.9 μ rad (55-20 μ rad in normal ops.)

Insertion Device Parameters

Betatron Function (β_x, β_y)	11.1 m, 5.84 m
Source Size (σ_x, σ_y)	1240 μ m, >45 μ m (130 μ m in normal ops.) *
Source Divergence (σ_x', σ_y')	112 μ rad, >7.7 μ rad (22 μ rad in normal ops.)

* ϵ_y is adjustable

OPERATIONS

BEAMLINE TECHNICAL IMPROVEMENTS

Roger Klaffky
Beamline Technical Liaison

As determined from the NSLS User Administration database statistics, there was a total of 2206 users working on scientific programs on both the X-Ray and VUV Storage Rings during FY 1995. The percentage breakdown of users according to home institution was 48.4 % from universities, 13.7% from abroad, 13.3% from industry, 8.3% from non-BNL DOE labs, 8.2% from BNL, 5.3% from government labs, and 2.7% from other U.S. institutions. Technical progress on the VUV and X-Ray beamlines is given below.

VUV BEAMLINES

There were a number of technical beamline improvements on the VUV Ring during FY 1995. At U2B there were developments on both the Spectra Tech scanning IR microspectrometer line and the Nicolet 750 IR spectrometer line for studies of materials at high pressures. The vacuum portion of the microspectrometer line was upgraded and new input optics were installed. The microspectrometer was commissioned for use with 15X and 32X objectives and tests were conducted in the Attenuated Total Reflection mode. A new optical system with improved signal throughput was installed on the high-pressure branch line, and the capability of accommodating larger cryogenic pressure cells was added.

At U4IR a new Michelson rapid-scan interferometer was tested in vacuum for future installation. This unit has dynamic alignment of the fixed mirror, to remove tracking errors in the moving mirror, and is capable of scanning at a more rapid rate, which is important in the far-IR. An upgrade of the existing Impact-400 Michelson interferometer electronics was also initiated.

As a result of an extensive study of the effect of U5U undulator gap changes on the VUV Ring, a program was developed which maintains the VUV Ring horizontal and vertical tunes essentially constant during + 2 mm gap changes. This has the effect of lowering orbit shifts to a level acceptable to UV users so that 30 minute advance notices are now required before U5U gap changes (as opposed to the prior 24 hour notice).

Modification of the U5 spin analyzer power sup-

plies significantly improved the energy resolution (at 30 eV photon energy) of spin-integrated spectra to 70 meV and of spin-resolved spectra to 100 meV.

The U5 diagnostic port was upgraded in several areas. A 2-D CCD camera with a Spiricon LBA-100 beam analyzer was put on line so that beam size history could be stored on the NSLS computer. A fast vacuum photo diode and sampling scope, which gave a bunch length averaged over thousands of beam revolutions, was replaced with a solid state photo diode, a 10 GHz pulse amplifier and a 5 GHz scope to measure bunch lengths during a single pass of beam.

During the winter 1994-5 shutdown, the U7A beamline was converted from a toroidal grating monochromator (TGM) to a spherical grating monochromator (SGM). The monochromator portion of the upgraded U7A beamline is optically identical to the U13UA and U4B SGMs. However, the collecting and focusing optic upstream of the monochromator is much different: the Kirkpatrick-Baez mirror pair, which is used in both the U13UA and U4B beamlines, is replaced by a single toroidal mirror. The slightly poorer focus produced by this toroidal mirror at the entrance slit of the SGM results in somewhat lower transmission through the entrance slit (but no degradation in photon energy resolution). However, this transmission loss is more than compensated for, in the soft x-ray region, by the elimination of one reflection. This new beamline geometry, dubbed the toroidal-mirror SGM (TSGM), has the advantages of no horizontal deflections (so it can fit in smaller angular space) and of permitting low-cost TGM→TSGM.

The multiparameter analyzer system, introduced on U9B in FY 1994 to measure the time dependence of fluorescence over a wide emission spectrum, was modified to permit determination of these quantities simultaneously for both vertically and horizontally polarized fluorescent light. The beamline control computer was upgraded to a 486 ISA computer.

A photo elastic modulator with a LiF optical element was tested on U11. This system permits measurement of circular dichroism to about 120 nm. Also, a superconducting magnet capable of reaching 7.5 Tesla

was tested. This magnet will be used to measure magnetic circular dichroism in the future. A U11 capital equipment project continued during FY 1995. The upgrade included improvements in: (1) computer hardware and software, (2) electronic and electrical equipment, and (3) the discharge flow-ionization mass spectrometer.

The two low energy (20-120 eV) Zeiss gratings (160 degrees included angle) were commissioned on U13UA during FY 1995. A resolving power of 5000 was demonstrated at 63 eV photon energy. On U13UB, light can be switched into any one of three instruments: a 20 reduction Schwarzschild camera operating at 6.8 and 13 nm; an "At-Wavelength" interferometer operating at 13 nm; or a 1X Offner imaging camera operating at 13 nm. The interferometer, commissioned during FY 1995, is capable of carrying out classical interferometry experiments at 13 nm. The 1X Offner camera, assembled and in an initial commissioning phase during FY 1995, will be capable of exposing wafers over a large (several square mm) area.

X-RAY BEAMLINES

A major change occurred in X-Ray operations in June 1995 when the maximum operational current increased from 250 mA to 300 mA. To prepare for the higher current, water-cooled beryllium windows were replaced on beamlines X4C, X6A, X6B, and X26A and nineteen white beam windows already in operation at 250 mA were checked for leaks. A new beryllium window design effort was underway in FY 1995 with the goal of installing 17 new windows during the December 1996 shutdown. Operations at 350 mA would commence in January 1997.

FY 1995 started off with a nagging problem with the liquid nitrogen transfer system which had slowed down to an excruciating fill time of 2.5 hours for a large dewar. This problem was remedied when an ice plug was thawed out by flowing warm helium gas through the transfer line, restoring fill times of less than 30 minutes.

There were a number of technical improvements on X-Ray beamlines during FY 1995. On the X3A1 and X3A2 beamlines new optics were put into operation. Additional improvements included stabilization of the A2 focused beam position at the sample using a second feedback loop to control the focusing mirror tilt. A miniature ion chamber is used for precise beam location. Also, a high energy Bonse-Hart ultra small-angle x-ray scattering instrument was constructed capable of operating at 0.65 Å.

The X4C beamline moved closer to an early commissioning phase with the acquisition of all the major

optical components. The variable focusing white beam mirror and mirror tank were assembled. The monochromator tank was delivered and fabrication of the monochromator bender and tilt and translation stages began.

On the X6A beamline, a new 4-point crystal bender was built which incorporates water cooling, crystal alignment and crystal tension release devices. These features will reduce aberration and increase stability. A new version of the beamline control software, EXAFS, was developed which includes procedures for polarization, magnetic circular dichroism (MCD) and synchronized laser measurements.

At X7B image plate data collection techniques were implemented for time-dependent powder diffraction. An image plate holder providing for controlled translation of the image plate past a slit, permitted the collection of complete series of powder patterns down to 10 second intervals. The X9A beamline was under construction. The hutch, photon shutter, primary aperture, and monochromator tank were completed.

The X11A hutch was expanded to make room for various experimental setups including a 13 element detector, UHV chambers, a large LN₂ dewar and a catalysis rig. The X11A motor driver system was converted from the Measurematic system to an ACS Step-Pak system. A more robust support was constructed for the Lytle detector to damp mechanical vibrations. The X11B double-bounce harmonic rejection mirror was mounted and characterized.

A new focusing mirror was installed on X12C which increased flux through a 200 micrometer aperture by a factor of 2.5.

At X15A two additional circles were added to the diffractometer, bringing it up to four-circle capability. Also, a hemispherical electron analyzer was installed on the UHV X-ray diffraction chamber.

A load lock was installed on the X16A beamline diffraction chamber to allow for fast sample switching of Si(111) experiments and to include chemical treatment steps in the surface preparation without breaking vacuum or losing alignment. At X16C a UHV surface EXAFS chamber was commissioned.

On the X17B2 angiography/MECT (multiple energy computed tomography) beamline the new patient chair, monochromator, filter and attenuator assemblies were used to image angiography patients. A new patient safety interlock system was also installed and tested. Beamline modifications resulted in the first MECT experiments being performed on phantoms and small animals in the imaging room.

New computer systems were acquired for the X18A beamline and optical encoders were integrated with the

monochromator. Software enhancements included improved backlash compensation for all motors. At X18B, a new monochromator was installed which covers the 7 KeV to greater than 50 KeV range using the Si(111) reflection. This is a water-cooled, detunable monolithic device providing simple, stable operation.

The X19A thin window system was installed. This system incorporates sensors and controls to close two fast valves in case of a window rupture. A number of other improvements were implemented. A goniometer system for performing single crystal x-ray absorption experiments was developed. A triple-bounce crystal system significantly enhanced the operation of the line at the sulphur K-edge by reducing the detuning required for harmonic rejection. Data collection software was implemented which may become a standard for NSLS x-ray absorption spectroscopy beamlines.

A high stability scanning stage was fully commissioned on the white beam topography camera on beamline X19C. This enables the recording of scanned images of very large single crystals in a single exposure. A routine experimental program began at X22A, a high-flux beamline for electrochemical studies. The X22B hutch was modified to accommodate a collaborator's 13 Tesla superconducting magnet. This entailed upgrades to the spectrometer table, radiation shielding, mu-metal shielding around the hutch and to the magnet sample holder. Also, a positive-feedback vibration isolator and three-fold increase in sample translation range were implemented on the liquid surface spectrometer.

At X23A2 the beamline computer system software was upgraded. The X23B upgrade to extend the energy range and to improve the focal spot continued with the successful testing of a prototype monochromator and the testing of new x-ray mirrors in BNL's Optical Metrology Shop. The mirror surface roughness was below 5 Å

At X24A, a new nickel-coated silicon primary spherical mirror was specified, procured and characterized (less than 3 Å RMS roughness). An increase of about two in flux delivered to the experimental chamber is expected at 3 keV. Better on-line alignment controls were implemented to ease the stringency of off-line pre-adjustment of monochromator crystals.

At X26A there was continued improvement of x-ray fluorescence and microbeam production instrumenta-

The new control room with NSLS Operations Staff: (counterclockwise from lower left) Lenny Pharr, Billy Jew, Tony Rodriguez, Mike Santana, and John Aloï.

tion. Work continued on developing and testing Kirkpatrick-Baez microfocusing mirrors. The K-B mirrors have produced x-ray beam sizes down to two microns with gains of about 1000 over pinhole-produced beams. A CCD camera system was tested for microtomography applications.

At X27C development of an x-ray microtomography facility began. The instrument relies on a cooled charge-coupled device imaging camera lens-coupled to a single crystal phosphor. A resolution less than 10 microns has been achieved with a 2mm × 2mm field of view.

A pinhole camera became operational at X28C and was interfaced to the accelerator control system, as a storage ring diagnostic. A slitted detector used with the x-ray pinhole also was used to study the frequency dependence of the beam size and beam position changes.

Thermal calculations performed on stainless steel fast valve blades indicated that the blades might melt after being fired and before the front mask would have time to close (which is about 0.7 seconds on X24). Since the X24A fast valve had fired a number of times during stored beam conditions, it was inspected during the May 1995 shutdown. The blade had a hole burned through it, as predicted from the calculations. The 8 mil stainless steel blades on X19A and X24A were then replaced with 10 mil thick molybdenum blades. A test to fire the X24 fast valve with currents above 400 mA was planned for just prior to the December 1995 shutdown.

A major improvement on the X-Ray floor was a building expansion between X1 and X12 which gave these beamlines more space by creating a walkway outside of the old building perimeter and provided these beamlines with new dedicated user labs. This same expansion provided a new expanded Control Room which began operation in September 1995 without any disruption to X-Ray operations.

OPERATIONS

X-RAY BEAMLINES

Roger Klaffky
X-Ray Operations Manager

The X-Ray Ring usage for FY 1995 is broken down in Figure 1. The percentage breakdown by categories is virtually the same as for FY 1994. There was a slight (1.6%) decrease in the operations percentage caused by the simultaneous failure of three of the four NWL Booster dipole power supply transformers in July. Operations were restored after the original Kirkoff supply was reactivated. Beam remained in the ring for 5 days, so that only 2 days of operations were lost. The transformers that failed had aluminum sheet windings with compression crimps on the copper power feeds. They had failed at the junction of the copper feeds and the aluminum sheet. New transformers were ordered with copper sheet windings and copper bars silver-soldered to the copper windings.

There was considerable activity on the X13 straight section during FY 1995. During the December 1994 shutdown, the NSLS Prototype Small Gap Undulator (PSGU) was removed so that vacuum chamber flanges could be re-machined to reduce the minimum electron beam aperture from 3.8 mm to 1.0 mm. The Elliptically

Polarized Wiggler (EPW) was installed in the X13 straight section during this same shutdown. The EPW began operation at 2 Hz in April after studies shifts had demonstrated that it had a negligible effect on users' beam. During the May 1995 shutdown trim magnets were installed to better compensate for vertical orbit motion caused by the EPW. The PSGU was reinstalled during the May 1995 shutdown and, in August, the photon spectrum showed that the design goal was achieved: a 2.5 keV fundamental, and a 7.5 keV third harmonic for a 2.5 mm electron beam aperture and a 5.6 mm magnet gap. The partial lifetime contribution was 36 hours. Shortly afterwards, the PSGU began operations at a 4.0 mm electron beam aperture and 7.5 mm magnet gap. Due to the reduction in beam lifetime at gaps less than 4mm, any operation at less than 4 mm will require approval by X-Ray users.

The maximum operational current of the X-Ray Ring increased from 250 mA to 300 mA at the end of June 1995. Before this boost in current could occur, a number of upgrades and tests had to be performed to comply with

Figure 1: The Breakdown of the X-Ray Ring usage based on total time (not scheduled time) for FY95.

Figure 2: The total integrated current for the X-Ray Ring accumulated each month for FY95.

the recommendations of the NSLS X-Ray Thermal Limits Task Force. Four water-cooled white beam beryllium windows were replaced and nineteen white beam windows already in operation at 250 mA were checked for leaks. Also, the X-Ray Ring active interlock system, with the exception of X13, was certified after the calibration and linearity of the system was verified up to 350 mA during 25 bunch operation. Finally, the front end masks on X21 and X25 were interlocked so they could not close unless the wiggler gaps were open. At the present time, operation of the ring up to 438 mA (at 2.584 GeV) or up to 250 mA at 2.8 GeV is possible during studies and template shifts. Beam lines having compatible beryllium windows and the proper radiation shielding will be allowed to operate during these shifts.

In order for operations to occur at currents above 300 mA for all beamlines, a sizeable number of beryllium windows will have to be replaced. Operation at 438 mA requires replacement of a total of 34 additional windows. A new beryllium window design effort was underway in FY 1995 with the goal of installation of 17 new windows during the December 1996 shutdown, which is halfway to the number required for 438 mA operation and more than required for 350 mA operation. Operations at 350 mA would commence in January 1997.

There was progress in further stabilizing the electron beam position and size during FY 1995. In late '94 the global feedback gain was increased by a factor of 3 at low frequencies and the bandwidth was increased from 60 Hz to 200 Hz. To avoid changes in horizontal and vertical beam size occurring at specific XRF2 tuner positions (i.e. higher order modes) during a fill, the XRF2 temperature ramp was adjusted. The XRF3 tuner temperature was adjusted so that its resonance occurred during the first hour after the fill which is the time that orbit corrections are made. Plans were made to attenuate these modes during the December 1995 shutdown. To track these beam size changes, the X28 profile monitor Spiracon was interfaced to the NSLS computer system to keep a daily history of beam size and position.

To enable high current operations, the X-Ray Ring

active interlock beam position monitor electronics were also upgraded. The AGC dynamic range was extended from 35 dB to 55 dB to allow prefill tests at 7 mA and to permit operations up to 434 mA. In the future, the improved electronics will be installed on the other ring bpms not in the active interlock system.

There were several successful trial runs of the digital orbit feedback system in the horizontal plane. The sampling frequency of the orbit micro was increased from

Roger Klaffky, X-Ray Ring Manager

60 Hz to 500 Hz to allow the digital feedback system to work. The higher sampling frequency will prove useful in diagnosing rapid orbit motion problems.

There were a number of steps taken to reduce downtime. A significant improvement resulted from running the RF systems with gap voltages adjusted so that if one system drops out, the three remaining systems can carry the beam load (up to 250 mA) without a beam dump. Also, the X-Ray Ring, VUV Ring, and Linac/Booster vacuum systems were placed on emergency power.

Considerable progress in the reliability of the NSLS water and compressed air systems was achieved by adding redundancy, and improving control and service ability. During the December 1994 shutdown, a third High Pressure Copper System water pump was installed allowing the pumps to operate within their design specifications. Pressure control was added to this system to maintain constant flow. The addition of cooling and compressed air from the BNL Central Chilled Water

Facility (CCWF) provided needed redundancy to the NSLS chillers and air compressors. The four NSLS chillers and air compressors have stood alone when the CCWF was down for maintenance/repair. Digital proportional integral controllers have significantly improved temperature control. Temperature jumps of 8 degrees F in the Low Pressure Copper water after an X-Ray dump or fill were reduced to 1 degree. Additionally, the RMS temperature changes in the water systems during stored beam conditions were reduced by a factor of 3 to 5. There was an ongoing effort to improve the serviceability of the proteus flow rate monitors by moving the proteus units from under the ring magnets and redesigning the plumbing to maintain a constant pressure boundary during testing and maintenance. To better track failure rates and pinpoint possible problems areas, there was implementation of color coding (according to time period of installation) of water and air hoses, and of an air solenoid inventory.

Finally, the new NSLS Control Room started up in September 1995, with no disruption to operations.

X-RAY STORAGE RING PARAMETERS AS OF NOVEMBER 1995

Normal Operating Energy	2.584 GeV
Maximum Operating Current	0.30 amp (10^{12} e)
Lifetime	~20 hours
Circumference	170.1 meters
Number of Beam Ports on Dipoles	30
Number of Insertion Devices	5
Maximum Length of Insertion Devices	< 4.50 meters
$\lambda_c(E_c)$ at 1.25 T (B)	2.23 Å (5.6 keV)
$\lambda_c(E_c)$ at 5.0 T (W)	0.56 Å (22.2 keV)
B(ρ)	1.25 Tesla (6.875 meters)
Electron Orbital Period	567.2 nanoseconds
Damping Times (2.584 GeV)	$\tau_x = \tau_y = 6$ msec; $\tau_z = 3$ msec
Touschek (2.584 GeV, 0.25A)	≥ 27 hrs ($v_{RF} = 700$ kV)
Lattice Structure (Chasman-Green)	Separated Function, Quad Triplets
Number of Superperiods	8
Magnet Complement	<div> <div>16 Bending (2.7 meters each)</div> <div>40 Quadrupole (0.45 meters each)</div> <div>16 Quadrupole (0.80 meters each)</div> </div>
32 Sextupole	(0.20 meters each)
Nominal Tunes (ν_x, ν_y)	9.15, 6.20
Momentum Compaction	0.0056
R.F. Frequency	52.88 MHz
Radiated Power for Bending Magnets	144 kW/0.25 amp of Beam
R.F. Peak Voltage	1000 kV
Design R.F. Power	400 kW
ν_s (Synchrotron tune)	0.002
Natural Energy Spread (σ_e/E)	8.6×10^{-4}
Natural Bunch Length (2σ)	10.5 cm
Number of RF Buckets	30
Typical Bunch Mode	25
Horizontal Damped Emittance (ϵ_x)	1.1×10^{-7} meter-radian
Vertical Damped Emittance (ϵ_y)	1×10^{-10} meter-radian
Power per Horizontal milliradian (0.25A)	23 watts

Arc Source Parameters

Betatron function (β_x, β_y)	1.0 to 3.8 m, 7.9 to 26.5 m
Dispersion function (η_x, η_y)	0.47 to -0.11, -0.39 to 0.22
$\alpha_{xy} = -\beta'_{xy}/2$	-0.49 to 1.62, -3.4 to 4.5
$\gamma_{xy} = (1 + \alpha_{xy}^2)/\beta_{xy}$	0.952 to 0.962 m ⁻¹ , 0.81 to 0.52 m ⁻¹
Source size (σ_x, σ_y)	371 to 565 μ m, 27 to 49 μ m
Source divergence (σ_x, σ_y)	439 to 324 μ rad, 8 to 7 μ rad

Insertion Device Parameters

Betatron function (β_x, β_y)	1.60 m, 0.35 m
Source divergence (σ_x, σ_y)	260 μ rad, 35 μ rad

Beamline U2B: A photograph of an inclusion in fluorite is shown above, and on the following page are maps of CO₂ (left) and oil (right) distribution in the inclusion. The locations of these two components are clearly seen inside the inclusion. The relative density is related to the local density. If the oil is homogeneous, the various intensities are related to the thickness of the areas probed. In addition, the frequencies of the modes change with pressure, opening up the possibility of determining the pressure-temperature situation when the inclusions were formed. Water can also be tested for, and in this case no water bands were detected inside the inclusion. [N. Guilhaumou (Laboratoire de Geologie, France) and P. Dumas (LURE-CNRS, Centre Universitaire, Paris-Sud)]

FIVE PROJECTS

High
Abs.

Low
Abs.

0
-10
-20
-30
-40
-50
-60
-70

-80 -60 -40 -20 0
microns

0
-10
-20
-30
-40
-50
-60
-70

-80 -60 -40 -20 0
microns

THE NSLS SOURCE DEVELOPMENT LABORATORY

Erik D. Johnson
SDL Project Manager

The NSLS has a deep interest in providing its user community with state of the art resources for their research, now and in the future. Beyond its immediate function of satisfying the requirements of the existing storage ring users, the NSLS must endeavor to anticipate and provide for needs which may be, as yet, unimagined. Although this activity can follow many threads, source development is clearly an area where considerable progress can be realized. FEL based sources hold the promise many orders of magnitude improvement in peak power over storage rings, and access to phenomena at sub-picosecond time scales.

For this reason, the NSLS has been engaged in the development of proposals for a Free Electron Laser user oriented facility operating in the Ultra-Violet for more than five years. This work culminated in the Deep Ultra-Violet Free Electron Laser (DUV-FEL) conceptual design report which was released in January of 1994. It details the scientific motivation, and describes a user facility designed to meet those needs. The DUV-FEL could produce picosecond pulses of UV radiation at wavelengths as short as 75 nm and peak power of several hundred megawatts. A subsequent development proposes FEL operation in a chirped pulse mode which could produce 4 femtosecond pulses at 88 nm with peak power of 100 GW.

Recognizing the potential impact of FELs on their core programs, the DOE commissioned the National Research Council to perform a study of Free Electron Lasers and Other Coherent Sources of Radiation to aid in evaluating their role in DOE programs. In its August 1994 report, the NRC panel recommended support for preliminary R&D to establish the feasibility of constructing a user oriented FEL in the VUV. Acting on this recommendation, the NSLS established the Source Development Laboratory (SDL). In broad terms, the function of the SDL is to facilitate the coordinated development of sources and experiments to produce and utilize coherent sub-picosecond synchrotron radiation.

The SDL accelerator system is located in building 729, and will consist of a high brightness short pulse linac, a station for coherent synchrotron and transition radiation experiments, a short bunch storage ring, and an ultra-violet free electron laser utilizing the NISUS wiggler. This accelerator will be realized by installing a photocathode electron gun of the type developed at the BNL-ATF on the existing 230 MeV linac. With the addition of a magnetic pulse compressor, the linac will supply 1nC bunches with a 100 μ m RMS σ length (ca. 1000 A peak current). As outlined in the 1994 NSLS annual report, the accelerator part of the SDL program can be thought of as occurring in three stages; all based on the production of short electron bunches:

- I 100 μ m Compressed Bunch Experiments
- II UP-FEL Ultraviolet Project Free Electron Laser
- III Compact Storage Ring with High Frequency RF.

For each of the sources, experiments utilizing the radiation they produce have been identified, and PI's from outside BNL have agreed to participate in early utilization of these sources while still under development. This close interaction between end users and source developers will help to focus research activities on the properties of the sources which will be most important for the research they are designed to enable.

The first stage of development represents establishment of the short pulse electron source and its characterization. One experiment planned with the recommissioned linac will utilize coherent transition radiation and an electron bunch to make pump-probe measurements of the response of highly excited dielectric media. This experiment also provides a method to diagnose and monitor the electron beam performance in subsequent experiments. The second stage is an incremental program of FEL source and experiment development which forms the centerpiece of the SDL program. It starts with Self Amplified Spontaneous Emission (SASE) operation of

the FEL which is, at least conceptually, the most straightforward type of single pass FEL. With the addition of an energy modulation wiggler and dispersive section, operation with an optically seeded beam becomes possible. This allows for shorter wavelength radiation through Harmonic Generation and increased pulse energy by Chirped Pulse amplification. These experiments will extend the range of FEL operation to wavelengths below 100 nm, and peak power exceeding 100 GW. The third stage, which may actually be carried on in parallel with the FEL program, explores the use of the short bunch beam in a storage ring. It represents a promising alternative to

laboratory and much of the hardware are recovered from various curtailed or terminated programs. The 230 MeV linac is derived from the DARPA SXLS project as is much of the storage ring. The 10 meter long NISUS undulator provides the amplifier for the FEL experiments. It was built by STI-Optronics for Boeing Space and Defense in Seattle as part of a contract with the US Army Space & Strategic Defense Commands Directed Energy Weapons Program. The FEL amplifier R&D component of the SDL is part of a broad based collaboration involving many institutions interested in the development of short wavelength FEL technology, as recommended by the NRC

report. Apart from BNL, this effort includes other DOE laboratories (CEBAF, LBL, LANL, SLAC), industrial partners (Boeing, Northrup Grumman, STI-Optronics), and universities (Duke, UCLA).

Activities during 1995 reflected the foundation phase for the SDL. Building 729 was expanded to accept the full SDL accelerator. The NISUS undulator was moved to its working location and connection of its control electronics was started. Reconfiguration of the linac and shielding was initiated as was planning for a clean room to house the laser systems. A Titanium:sapphire laser was specified and procured to drive the photocathode gun, and in

future, act as a seed laser. Assembly of the electron linac is scheduled to be completed, with parallel activities in design and commissioning of equipment for the FEL and storage ring experiments. With the assembly of the accelerator well underway, the SDL will be an increasingly visible activity during 1996. Those of us directly associated with the project look forward to starting experiments in the following year.

Pictured in position at the Source Development Laboratory (SDL) with the National Synchrotron Light Source (NSLS) in the background, NISUS is being inspected by some of those at the NSLS involved in putting SDL together and planning its future experiments: (from left) Physicist Ilan Ben-Zvi; Erik Johnson, SDL Project Manager; Physicist Li-Hua Yu; and Samuel Krinsky, NSLS Deputy Chairman.

FELs or conventional storage rings as a source of coherent radiation in the far-infrared. In this case the storage ring is the recovered XLS ring, modified to provide coherent radiation at 300 μ m wavelengths and longer. This is accomplished by reconfiguring the ring to operate with a high frequency RF system, and a reduced momentum compaction lattice.

Given the fiscal realities of today, the SDL program has been structured to utilize existing equipment to the greatest extent possible, and encourage collaboration both within and outside of BNL. To that end, the site for the

PROJECTS

THE ACCELERATOR TEST FACILITY

Ilan Ben-Zvi

The NSLS has an active program in R&D in the production of short-wavelength coherent radiation through its involvement in the Accelerator Test Facility.

The Accelerator Test Facility (ATF) is a User's Facility for accelerator and beam physicists, operated by the NSLS and the BNL Center for Accelerator Physics. There is no other peer-reviewed facility like the ATF that is dedicated for long range R&D in accelerator and beam

the ATF, there is a number of FEL experiments. A few of them are centered about ATF beam line #3, where a microundulator oscillator experiment is nearing operation and others are conducted on beam line #2, like the High Gain Harmonic Generation FEL.

A superconducting 68 period micro-undulator (with a period of 0.88 cm and 0.5 Tesla peak field at a gap of 0.44 cm) has been developed at the NSLS. Prototypes of

this undulator (up to 23 periods long) were built and performed extremely well in superconducting tests. The field errors of the undulator were very low as constructed, making this perhaps the first undulator that will require no trimming after manufacture. The FEL experiment makes use of the short period of the undulator and the low emittance beam generated by the RF photocathode gun to operate at 500 nm with a 50 MeV electron beam. Since the ATF electron beam energy is currently at about 70 MeV, lasing at below 250 nm should be possible. The technology developed for this undulator will be used to develop a 4 to 5 mm period, small gap undulator prototype for the National Synchrotron Light Source X-Ray Ring.

Ilan Ben-Zvi at the Accelerator Test Facility's experiment hall.

physics. In addition to its singular role, the ATF also has a unique combination of a high-brightness electron beam, synchronized high power lasers, and a well equipped, 3 beamline experiment hall. The high brightness electron beam of the ATF, produced by a laser-photocathode RF gun, makes it an ideal site for R&D on Free-Electron Lasers (FEL).

Among the 15 currently approved experiments on

An MIT group is carrying out a test of a pulsed microundulator. This undulator, which is currently installed on the beam line, has parameters that are very similar to those of the superferric undulator. Spontaneous emission has already been observed from this device and preparations are under way to get lasing in the near future. A third user group is from Columbia University. They will be using the oscillator experiment for studies of

spiking and optical guiding in FELs.

The high-gain harmonic-generation experiment will be located on beam line #2. This experiment is carried out by a NSLS group headed by Li-Hua Yu. The experiment is done in collaboration with Northrop - Grumman, which is providing many components of the undulator for the experiment. This undulator is a derivative of the superconducting micro-undulator of the visible FEL oscillator. It uses the same principle of a continuous yoke but has parabolic pole faces for two-axis focusing and four distinct regions: a prebunching undulator, a dispersive section, an exponential growth section and a tapered section. This experiment emulates the FEL physics of the NSLS approach to VUV FELs. This approach is based on single pass, seeded FEL amplifiers driven by Ti:sapphire lasers. The final stage of harmonic generation is being done in the FEL. The principle of high gain harmonic generation will be tested and characterized in these experiments, as well as the superconducting undulator, the undulator diagnostics, error and alignment studies and tapering control.

Another experiment at beam line #2 has recently broken the world record for Inverse FEL acceleration of electrons. This experiment, headed by Arie van Steenbergen, used the high-power CO₂ laser of the ATF and a special variable period wiggler to impart 2% acceleration to a 40 MeV beam, using about 0.5 GW of the CO₂ laser. This experiment, which is like an FEL amplifier operated in reverse, is motivated by the interest to develop a compact, high-gradient electron accelerator.

The development of a high brightness electron beam is essential to the production of coherent short wavelength radiation. The length of both accelerator and wiggler of the FEL will decrease sharply with improved beam brightness. In a remarkable case of parallel evolution, this work is also important to High Energy Physics for the construction of future linear colliders. Thus the ATF is enjoying considerable support from the DOE office of High Energy Physics. R&D at the ATF on the generation of high brightness beam placed the NSLS in an international leadership position. The electron gun of the ATF generates its high current, low emittance beam by irradiating a high-quantum-efficiency metal-cathode in the presence of very high intensity RF electric fields. The generation and careful manipulation of such beams are areas of intense activity in accelerator physics, being the key to short wavelength FELs. A new magnesium photocathode has demonstrated an order-of-magnitude increase in quantum efficiency with a (so far) unlimited lifetime. The ATF is leading two new collaborations for the development of RF guns, one with SLAC and UCLA, and the other with Japan, KEK and Sumitomo.

Two significant experiments have been recently reported by the ATF staff. The first is a measurement of the slice-emittance of an electron bunch from the ATF electron gun. This newly developed technique makes it possible to study in detail the longitudinal dependence of the transverse beam-matrix of short slices with 1 picosecond resolution. The slice-emittance measurement enabled us to examine the evolution of the beam while it goes through the important emittance-compensation process. Emittance compensation is a linear correlation-removal process that has led to the improvements in photocathode RF gun beam brightness and to the recent enhanced interest in x-ray FELs. The slice-emittance measurement should allow us to do non-linear emittance corrections that promise even better x-ray FELs. The second development is the observation of micro-bunching of the ATF's beam. Under certain conditions it is possible to obtain sub-picosecond long bunches with a high charge and good emittance. This happens when the photocathode laser is adjusted to a small phase, leading to bunch compression in the drift space between the gun and the linac. One picosecond bunch lengths have been measured (using a variation of the slice emittance set-up). Much shorter bunches are predicted theoretically, but await a further refinement of Eric Blum's coherent radiation detector. Eric has already observed coherent radiation from the ATF's beam. An installation of a spectrometer will allow sub-picosecond bunch length measurement.

As a result of the bunch compression, the bunch length of the ATF can be changed easily from about 10 picoseconds to under one. If this bunch is collided with an energetic pulse from the ATF's synchronized CO₂ laser, a pulse with the same short length of X-rays is produced. Compton back-scattering of lasers by electrons is a unique X-Ray source. Preliminary estimates indicate that it should be possible to generate elliptically polarized 2×10^8 photons pulse of 8 KeV x-rays using the ATF's future 1 TW CO₂ laser and its 70MeV linac. A contract for the construction of parts for the ATF's compact picosecond Terawatt laser was signed last year.

In a significant contribution to the education of future generation of accelerator physicists, eight graduate students have finished their thesis at the ATF and six others (from Columbia, Dartmouth, MIT, Stanford, Stony Brook and UCLA) are currently doing thesis research at this facility. More information on the ATF can be found on the World Wide Web, with a hyperlink from either the National Synchrotron Light Source or BNL Home Pages.

NSLS FACILITY IMPROVEMENTS

Frank Terrano
Mike Kelly

FY 1995 saw the completion of two construction initiatives along with several other facility related projects. The successful completion of these efforts has allowed us to make further progress toward our goals of enhancing the research environment, and generally making the NSLS a friendlier place for users to visit.

In March of 1995 the NSLS took occupancy of the Structural Biology addition. The 6,300 square foot addition includes laboratories for X11, X10, X9, X8C, X6, and X3B1 shared with X7. It also houses a general user structural biology laboratory with a cold box, a general user laboratory, and a conference room. X9 and X8C have a shared cold box located between their laboratories.

In December the NSLS took occupancy of the X1-X4 Control Room addition. This addition includes a laboratory for X4 with cold room, laboratories for X1A and X2, and storage/setup space for X1B and X3. It also includes a new NSLS control room, almost doubling the size of the old one. The NSLS Safety Group and Building Manager now occupy this space close to the new control room. The old control room will house the off duty Operations Coordinators. The NSLS User shop, previously at the other end of the tunnel in building #535 has moved up onto the experimental floor, making it closer to the setup space and stockroom.

Every beamline will now have a laboratory or setup/storage area to support their operations.

Structural
Biology
Addition

X1-X4 Control Room Addition

The connection of the NSLS building to the Central Chilled Water Facility was completed. This will add greater flexibility as well as redundancy capabilities to the machine and comfort cooling of the facility. The final phase which will be to add connections for the experimental water system is expected to be completed in FY 1996.

In May 1995, a Superconducting Magnet Energy Source (SMES) was installed for testing on the NSLS VUV Ring. Acquired from the U.S. Air Force, the system is housed in a standard trailer adjacent to the east side of building 725. The SMES is designed to cut in when an AC power disturbance is detected and is expected to

handle at least a 2 second power outage of the VUV Ring with all its ancillary components. This should enable us to ride out LILCO power fluctuations which would have previously dumped the beam. After about a year or so testing, a decision will be made as to whether to place the entire facility on the SMES system.

Building 729, the Source Development Laboratory, was extended forty feet to house the NISUS wiggler and Linac tandem. A chiller was plumbed into the building which will handle machine cooling and comfort cooling of the facility.

Dedication of the NSLS Structural Biology addition on May 10, 1995: Roland Hirsch from the DOE Office of Health & Environmental Research (far right) was joined by (left to right) BNL Laboratory Director Nicholas Samios, Denis McWhan (BNL Associate Director for BES/Acting NSLS Chair) and William Studier (BNL Biology Department Chairman) for a ceremonial ribbon cutting.

Eric Sirota (Exxon Research & Engineering Co.) and Helmut Strey (NIST) in one of the new laboratories on the NSLS experimental floor.

Beamline X26A: The upper image is a photograph of a 4 x 4 mm area of a rice leaf. The greenish-yellow areas are healthy leaf tissue; the horizontal lines are veins. The dark area to the right of center is a fungal lesion, a site at which *P. grisea* has attacked the leaf. The edge of a second lesion is just visible along the bottom edge of the photograph. The lower image is a map of Mn oxidation state obtained using micro-XANES spectroscopy. Yellow indicates the presence of only Mn^{2+} , while red and blue indicate progressively greater Mn^{4+} contents. [D. Schulze (Purdue University)]

SIX **ORGANIZATION**

Increasing Mn oxidation →

NSLS ADVISORY COMMITTEES

1995-1996

Users' Executive Committee

The Users' Executive Committee (UEC) provides for organized discussions among the user community, NSLS administration, and laboratory directorate. It aims to communicate current and future needs, concerns, trends within the user community to NSLS staff and management, and to disseminate to the users information about NSLS and BNL plans. Members were:

Chairperson: Paul Zschack, ORNL

Vice-Chairperson: Peter Stephens, SUNY-Stony Brook

Past -Chairperson: Jean Jordan-Sweet, IBM

Secretary: Sue Wirick, SUNY-Stony Brook

Daniel Fischer, NIST

Doon Gibbs, BNL-Physics

Kim Mohanty, BNL-Physics

Kevin Smith, Boston U.

Ex-Officio: Eva Rothman, NSLS

Special Interest Group Representatives

Special interest groups in areas of common concern communicate with NSLS management through the UEC. Group representatives were:

Atomic and Molecular Science	David Hanson, SUNY- Stony Brook
Biological Scattering, Crystallography	Stephan Ginell, ANL
Energy Dispersive Diffraction	Syed Qadri, Naval Research Lab
Imaging	Sue Wirick, SUNY- Stony Brook
Nuclear Physics	Craig Thorn, BNL-Physics
Students and Post Docs	David Johnson, BNL-Chemistry
Time Resolved Spectroscopy	Jon Levin, U. of Tennessee
Topography	Michael Dudley, SUNY-Stony Brook
UV Photoemission, Surface Science	Boris Sinkovic, NYU
XAFS	Simon Bare, Dow Chemical
X-Ray Scattering , Crystallography	Ben Ocko, BNL-Physics

Science Advisory Committee

The Science Advisory Committee (SAC) evaluates the science programs at the NSLS and makes recommendations to the Chairman. The SAC met in March of 1995 and its members were:

B. Batterman, CHESS, Cornell U.
Gene Dresselhaus, National Magnet Laboratory, MIT
Richard Martin, Department of Physics, U. of Illinois
Yves Petrof, ESRF
David Shirley, Penn State University
Janet Smith, Department of Biological Science, Perdue U.
Chandra Varma, AT&T Bell Laboratories

General User Proposal Study Panels

The Proposal Study Panels met in November 1994, March 1995, and July 1995 to review and rate General User research proposals for the FY 1995 cycles. PSP members are drawn from the scientific community and usually serve a two year term. Members during FY 1995 were:

UV Panel

Steve Hulbert	NSLS
Theodore Madey	Rutgers U.
Cliff Olson	Ames Laboratory
John Sutherland	BNL-Biology

X-Ray Imaging/Other Panel

Harold Ade	NCSU
Jamshed Patel	AT&T
Bruce Steiner	NIST

X-Ray Biology

Stephen Burley	Rockefeller U.
Keith Watenpugh	The Upjohn Co.

X-Ray Spectroscopy Panel

Bruce Bunker	U. of Notre Dame
John Faber	Amoco
Ronald Felton	Georgia Inst. of Tech.
William Orme-Johnson	MIT
James McBreen	BNL-DAS
Lynn Soderholm	ANL
Dale Sayers	NCSU
Ed Stern	U. of Washington

X-Ray Scattering Panel

Malcolm Capel	BNL-Biology
Ben Chu	SUNY - Stony Brook
Philip Coppens	SUNY - Buffalo
Charles Prewitt	Geophysical Lab
Robert Fleming	AT&T
Simon Moss	U. of Houston
Ian Robinson	U. of Illinois
Cullie Sparks	ORNL

General User Oversight Committee

The General User Oversight Committee (GUOC) met in November 1994, March 1995, and July 1995 to allocate time on beamlines to each General User proposal for the FY 1995 cycles. GUOC members are drawn from the scientific community and usually serve a two year term. Members during FY 1995 were:

UV Members

C.T. Chen	AT&T
Brian DeVries	Exxon
Jan Hrbek	BNL-Chemistry
Eric Jensen	Brandeis U.
Boris Sinkovic	NYU
Paul Stevens	Exxon

X-Ray Members

David Adler	AT&T
Alex Darovsky	SUNY-Stony Brook
Kegang Huang	ANL
Simon Mochrie	MIT
Benjamin Ocko	BNL-Physics
William O'Grady	NRL
Peter Stephens	SUNY-Stony Brook
Joseph Woicik	NIST

ORGANIZATION

NSLS STAFF

- * Temporary
- ** Reports to Denis McWhan,
Assoc. Dir. for Basic Energy Sciences
- () PRT personnel or member of non-NSLS division

ORGANIZATION

NSLS STAFF

(signed) Michael Hart, Chairman

April 1, 1996

ORGANIZATION

VUV BEAMLINE GUIDE

Beam line	Research Program	Mono.	Affiliation	Local Contact	Spokesperson
U1A	SEXAFS, ARUPS, XPS	ERG	Exxon	B DeVries 516-344-4828 516-344-5206	J Chen 908-730-2738
U1B	(Conceptual)	TGM	Exxon	B DeVries 516-344-4828 516-344-5206	P Stevens 516-344-4828 908-730-2584
U2A	(Unassigned)				
U2B	High pressure, pump-probe, high Tc abs., IR microscopy	MI	SUNY@SB BNL-NSLS Northrop Grumman	G Williams 516-344-7529	G Carr 516-344-5502 516-346-9073
U3A	Time-resolved and DC radiometry; reflectometry for optical constants	ERG	Los Alamos Natl Lab Smiths Astro Obs Bechtel Nevada	W Towell 516-344-7245	R Blake 516-344-5521 505-983-9683
U3B	(Conceptual)				
U3C	Photoelectron spect.; exp. system and detector calibrations	ERG	Los Alamos Natl Lab Sandia Natl Lab	W Towell 516-344-7245	R Bartlett 516-344-5708 505-667-5923
U4A	ARUPS of solids, surfaces; hi res. core level photo-emission; total yield absorption	TGM	AT&T BNL - NSLS Boston U	M Shek 516-344-5930	J Rowe 908-582-5878
U4B	Soft x-ray photoemission spectroscopy; NEXAFS; SXMCD	SGM	AT&T Naval Res Lab	G Meigs 516-344-7290 908-582-3863 Y Idzerda 202-767-3603	

Beam line	Research Program	Mono.	Affiliation	Local Contact	Spokesperson
U4IR	Vibr. spectr of molecules on surfaces; abs of hi Tc superconductors; hi res gas abs.; fast detectors	MI,WDI	BNL-NSLS AT&T Fairleigh Dickinson Exxon Northrop-Grumman ATDC	D Van Campen 516-344-2738 516-344-7419	G Williams 516-344-7529
U5	Diagnostics		BNL-NSLS	R Nawrocky 516-344-4449	R Nawrocky 516-344-4449
U5U	Spin polarized angle- resolved ultraviolet photoemission	TGM	BNL-NSLS	S Hulbert 516-344-7570 E Vescovo 516-344-7399	E Vescovo 516-344-7399
U6	Lithography	WB	IBM	J Silverman 914-945-2099	J Silverman 914-945-2099
U7A	Photoemission; SEXAFS; Fluorescence yield spectroscopy	TGM	BNL-NSLS BNL-Physics BNL-Chemistry Dow Chemical NIST U of Michigan	Q Dong 516-344-5505 516-344-5507 S Hulbert 516-344-7570	D Fischer 516-344-5177
U7B	Photoemission; SEXAFS	PGM	BNL-Physics SUNY@SB	F Loeb 516-344-2092	M Strongin 516-344-3763
U8A	ARUPS NEXAFS	TGM	IBM	R McFeely 914-945-2068	R McFeely 914-945-2068
U8B	ARUPS NEXAFS	TGM	IBM	R McFeely 914-945-2068	R McFeely 914-945-2068
U8C	Zone plate monochr evaluation; reflectivity measurements of thin films and multilayers	ZONE PL.	IBM	R McFeely 914-945-2068	R McFeely 914-945-2068
U8D	(Conceptual) Scanning soft x-ray microscopy		IBM	R McFeely 914-945-2068	R McFeely 914-945-2068
U9A	(Planned) Lithography			F Loeb 516-344-2092	M Strongin 516-344-3763

Beam line	Research Program	Mono.	Affiliation	Local Contact	Spokesperson
U9B	CD; MCD; time-resolved fluorescence (lifetimes)	C-T	BNL-NSLS BNL-Biology	J Sutherland 516-344-3406 516-344-3279	J Sutherland 516-344-3406 516-344-3279
U10A	(Unassigned)				
U10B	PSD - general vacuum R&D	WB	BNL-NSLS	C Lanni 516-344-4100	C Foerster 516-344-4754
U11	Gas phase photo- ionization and Spectroscopy	NIM	BNL-NSLS BNL-Biology Brandeis U BNL-DAS	S Kuo 516-344-7003	B Klemm 516-344-4001 516-344-4022
U12	High resolution core level Spectroscopy ARUPS	TGM	U of Pennsylvania Oak Ridge Natl Lab	P Lyman 516-344-5615 516-344-7395	E Plummer 615-974-2288 D Zehner 516-344-5512 615-574-6291
U12A	High resolution core level spectroscopy (construction)	TGM	Oak Ridge Natl Lab U of Tennessee	P Lyman 516-344-5615 516-344-7395	E Plummer 615-974-2288 D Zehner 516-344-5512 615-574-6291
U12B	Angle-resolved photoemission	TGM	Oak Ridge Natl Lab U of Tennessee	P Lyman 516-344-5615 516-344-7395	D Zehner 516-344-5512 615-574-6291 E Plummer 615-974-2288
U13UA	High res. VUV/soft XAS and electron spectroscopy (incl. spin-pol photoem.)	SGM	BNL-NSLS Drexel U U of Wisconsin Brandeis U Rutgers U NYU	S Hulbert 516-344-7570 X. Wu 516-344-5778	S Hulbert 516-344-7570
U13UB	Optical metrology for extreme ultraviolet projection lithography	WB	Sandia Natl Lab BNL-Instrum Naval Res Lab	A MacDowell 516-344-5334	A. MacDowell 516-344-5334

Beam line	Research Program	Mono.	Affiliation	Local Contact	Spokesperson
U14A	Solid state photoemissions studies	PGM	BNL-NSLS	M Shek 516-344-5930 S Hulbert 516-344-7570	M Shek 516-344-5930
U14B	Detector Research and Development	WB	BNL-NSLS	J Hastings 516-344-3930	J Hastings 516-344-3930
U15	Soft x-ray spectroscopy (solids and gases)	TGM	BNL-NSLS SUNY@SB SUNY@Buff	D Hanson 516-632-7917	D Hanson 516-632-7917
U16A	(Unassigned)				
U16B	ARUPS; XPS; SEXAFS; stimulated desorption; NEXAFS	ERG	Cornell U Sandia Natl Lab		R Merrill 607-255-9857

ORGANIZATION

X-RAY BEAMLINE GUIDE

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X1A	Soft x-ray imaging	10-80 Å	BNL-NSLS SUNY@SB LBNL No Carolina St U ANL	S Wirick 516-344-4723 516-632-8095	J Kirz 516-344-4723 516-632-8106
X1B	Soft x-ray spectroscopy	10-50 Å	BNL-NSLS BNL-Physics FA - Juelich Fritz-Haber-Inst	P Johnson 516-344-3705	P Johnson 516-344-3705
X2A	Surface scattering		Exxon	M Sansone 201-730-3388 516-344-5759	K Liang 908-730-3032
X2B	X-ray microtomography	6.5-30, WB	Exxon	K Mohanty 516-344-4402	D Noh 908-730-2598
X3A1	Short wavelength crystallography, diffraction and scattering	14, 19, 31	SUNY@SB SUNY@Buff	A Darovsky 516-344-3770	P Coppens 716-645-6800 ext. 2217
X3A2	Diffraction; x-ray spectroscopy; scattering; crystallography; small angle scattering	3-31	SUNY@SB SUNY@Buff	A Darovsky 516-344-3770	P Coppens 716-645-6800 ext. 2217
X3B1	X-ray spectroscopy; powder diffraction	4.6-40	SUNY@SB SUNY@Buff	P Stephens 516-344-5634 516-632-8156	P Coppens 716-645-6800 ext. 2217
X3B2	Surface science	4-20	SUNY@SB SUNY@Buff	P Stephens 516-344-5634 516-632-8156	P Coppens 716-645-6800 ext. 2217
X4A	Multiwavelength anomalous diffraction analysis of crystalline biological macromolecules	4-30	Howard Hughes Med In	C Ogata 516-344-7435	W Hendrickson 516-344-4938 212-305-3456

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X4B	(Conceptual)				
X4C	Diffraction measurements from biological macromolecules	7-20	Howard Hughes Med In	C Ogata 516-344-7435	W Hendrickson 516-344-4938 212-305-3456
X5A	Laser Electron Gamma Source (LEGS); medium energy nuclear physics	80-400 MeV	BNL-Physics	C Thorn 516-344-7798	A Sandorfi 516-344-7951
X5B	Diagnostic				
X6A	Time and space resolved dispersive x-ray spectroscopy	4-20	ANL	P Lee 516-344-5934 516-344-3955	P Montano 708-252-6239
X6B	X-ray scattering	2.4-21.0	ANL Temple U Northwestern U BP	P Lee 516-344-5934 516-344-3955	P Montano 708-252-6239
X7A	Structural char. through powder diffraction	5-45, WB	BNL-NSLS BNL-Physics Carnegie Inst of Was E I DuPont Mobil UOP Air Products Corp SUNY@SB/Alfred U of Cal @ Santa Barbara U of Pennsylvania	D Cox 516-344-3818 Q Zhu 516-344-3818 516-344-5065	D Cox 516-344-3818
X7B	Crystallography; wide angle scattering	5-21	BNL-Chemistry Swedish Nat Res Coun U of Pittsburgh U of Helsinki	J Hanson 516-344-4381 516-344-4378	T Koetzle 516-344-4384
X8A	Photoionization cross- sections; photoelectron spectr; mirror reflect; detector calib.; spectr.	0.26-5.9	Los Alamos Natl Lab Smiths Astro Obs EG&G Energy Meas Bechtel Nevada	M Sagurton 516-344-5708	R Blake 516-344-5521 505-983-9683
X8C	Diffraction from biological macromolecules and detector calibrations	5-20	Los Alamos Natl Lab Sandia Natl Lab LLNL ANL	R Alkire 516-344-5025	G Idzorek 516-344-7245 505-667-8848
X9A	XAS	3.4-18.6	Albert Einstein College of Medicine	M Sullivan 516-344-3800	M Chance 516-344-3800 718-430-2894

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X9B	Time resolved x-ray spectroscopy; scattering; diffraction; XAS	3.2-18.8	Albert Einstein College of Med	M Sullivan 516-344-3800	M Chance 516-344-3800 718-430-2894
X10A	Diffraction; small angle scattering; crystallography; scattering	6-15.2	Exxon	E Sirota 908-730-3407	K Mohanty 516-344-4402
X10B	Scattering; crystallography	8, 12	Exxon	D Noh 908-730-2598	B Zhang 516-344-3553
X10C	EXAFS	3.5-24.7	Exxon	M Sansone 516-344-5759 201-730-3388	P Stevens 516-344-4828 908-730-2584
X11A	EXAFS	4.5-35	No Carolina St U U of Connecticut BNL-NSLS Naval Res Lab Mobil E I DuPont Hoechst Celanese Naval Surf Warf Center Notre Dame U U of Washington Ill Inst of Tech Georgia Inst of Tech Rice U ANL	G Lamble 516-344-7734	G Lamble 516-344-7734
X11B	EXAFS	1.7-8	No Carolina St U U of Connecticut BNL-NSLS Mobil E I DuPont Naval Res Lab Hoechst Celanese Naval Surf Warf Center Notre Dame U U of Washington Ill Inst of Tech Georgia Inst of Tech Rice U ANL	G Lamble 516-344-7734	G Lamble 516-344-7734
X12A	Instrument development		BNL-NSLS	DP Siddons 516-344-2738 516-344-5627	DP Siddons 516-344-2738 516-344-5627
X12B	Time-resolved and static x-ray diffr. of macromol. systems in both wide and small angle regimes	6-15	BNL-NSLS BNL-Biology	M Capel 516-344-5712	M Capel 516-344-5712

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X12C	Protein crystallography	7.8-13.6	BNL-Biology	R Sweet 516-344-3401	R Sweet 516-344-3401
X13	R&D optics development; soft x-ray utilization		BNL-NSLS	E Johnson 516-344-4603	E Johnson 516-344-4603
X14A	Scattering; crystallography; spectroscopy	3.5-40	Oak Ridge Natl Lab U of Illinois	T Gog 516-344-5614 516-344-2583	T Gog 516-344-5614 516-344-2583
X14B	(Conceptual) X-ray microprobe; x-ray micro-focussing; micro-diffraction	WHITE	Oak Ridge Natl Lab	T Gog 516-344-5614 516-344-2583	T Gog 516-344-2583 516-344-5614
X15A	X-ray standing waves	3-20, WB	ANL Northwestern U Harvard U	P Lyman 516-344-5615 516-344-7395	M Bedzyk 516-344-7395 708-252-7763
X15B	SEXAFS EXAFS NEXAFS	1.5-15	AT&T	L Niu 908-582-5275 A MacDowell 516-344-5334	P Citrin 908-582-5275
X16A	Surface diffraction	4-12	AT&T U of Illinois	K Evans-Lutterodt 516-344-2125 908-582-2154	K Evans-Lutterodt 516-344-2125 908-582-2154
X16B	Diffraction	7.85	AT&T	A MacDowell 516-344-5334	E Isaacs 908-582-7261
X16C	Novel spectroscopy; diffraction	3-16	AT&T U of Illinois	D Adler 516-344-2686	W Brown 908-582-3941
X17A	(Conceptual)				
X17B1	Chemical crystallography; hi P physics; tomography; x-ray scattering; x-ray fluorescence microprobe	10-100, WB	BNL-NSLS	DP Siddons 516-344-2738 516-344-5627	J Hastings 516-344-3930

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X17B2	Medical research: Angiography; computed tomography; radiotherapy	33.02,33.3	BNL-NSLS Stanford U Illinois Inst Tech No Shore U Hosp LBNL BNL-Medical SUNY@SB	N Gmür 516-344-2490	W Thomlinson 516-344-3937
X17C	Hi P research; energy dispersive diffraction from microscopic sample volumes	10-100, WB	Naval Res Lab Carnegie Inst of Was U of Hawaii U of Chicago LLNL	J Hu 516-344-5343 202-686-2410	H Mao 202-686-2410 ext. 2467
X18A	Diffuse and surface scattering	4-20	Purdue U Northwestern U U of Illinois U of Missouri	S Ehrlich 516-344-7862	G Liedl 317-494-4100
X18B	EXAFS; optics char.; reflectivity measurements	4-26	BNL-NSLS AlliedSignal UOP Chevron	DP Siddons 516-344-2738 516-344-5627	DP Siddons 516-344-2738 516-344-5627
X19A	X-ray Absorption Spect.; EXAFS and XANES	2.1-25.6	BNL-NSLS UCA@Davis U of Kentucky U of Michigan BNL-DAS	F Lu 516-344-2338 L Furenlid 516-344-5699	L Furenlid 516-344-5699
X19C	Topography; liquid surface scattering	4-25, WB	BNL-NSLS SUNY@SB Johns Hopkins U Army Research Lab U of Illinois U of Chicago	M Dudley 516-632-8500	M Dudley 516-632-8500
X20A	Scattering (hi Q-res)	5.6-12	MIT		S Mochrie 617-253-6588
X20B	Scattering at fixed energy	17.36	IBM MIT	J Jordan-Sweet 516-344-5192 914-945-3322	S Mochrie 617-253-6588
X20C	Scattering (hi and low Q res)	4-11	IBM	J Jordan-Sweet 516-344-5192 914-945-3322	J Jordan-Sweet 516-344-5192 914-945-3322

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X21	High energy resolution inelastic scattering	> 4	BNL-NSLS AT&T BNL-Physics SUNY @ Stony Brook ESRF ANL	C Kao 516-344-4494 W Caliebe 516-344-4795	C Kao 516-344-4494
X22A	In-plane diff. & refl. studies of surfaces under electro-chem. cond., and thin films and multilayer	10 Nom.	BNL-Physics BNL-DAS	T Thurston 516-344-3761 B Ocko 516-344-4299	D Gibbs 516-344-4608
X22B	High resolution x-ray diffraction	5-10	BNL-Physics Harvard U ANL	B Ocko 516-344-4299 J Hill 516-344-4370 516-344-3736	D Gibbs 516-344-4608
X22C	Diffraction studies of magnetic and structural phase transformations; surface scattering	3-12	BNL-Physics ANL	D Gibbs 516-344-4608 G Watson 516-344-2211	D Gibbs 516-344-4608
X23A2	EXAFS	5.4-30	NIST	J Woicik 516-344-5823 516-344-5236 S Chu 516-344-3923 301-975-5975	J Woicik 516-344-5236 516-344-5823
X23A3	Topography; small- angle scattering	5-30, WB	NIST	D Fischer 516-344-5177	G Long 301-975-5975
X23B	EXAFS; scattering; crystallography	3-11	Naval Res Lab	J Kirkland 516-344-2258	T Elam 202-767-3014
X24A	Atomic, molecular, and optical physics with x-rays	1.8-5.0	NIST ANL	R Deslattes 301-975-4841	R Deslattes 301-975-4841
X24C	Photoemission and reflectance spectroscopy	2-1500 eV	Naval Res Lab	J Rife 202-767-4654	M Kabler 202-767-2223
X25	High Q-resolution elastic scattering	> 3	BNL-NSLS	L Berman 516-344-5333	L Berman 516-344-5333

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X26A	Dev. and application of analytical techniques (e.g. microprobe)	4-20, WB	BNL-DAS U of Chicago U of Georgia BNL-Biology	S Bajt 516-344-5596	S Sutton 312-702-9930
X26C	Dev. and applic. of x-ray microscopy techniques; Laue diffraction protein crystallography	4-30, WB	BNL-DAS U of Chicago BNL-Biology U of Georgia	G Shea-McCarthy 516-344-2229	S Sutton 312-702-9930
X27A	Instrument development		BNL-NSLS	DP Siddons 516-344-2738 516-344-5627	DP Siddons 516-344-2738 516-344-5627
X27B	Instrument development		BNL-NSLS	E Johnson 516-344-4603	E Johnson 516-344-4603
X27C	Instrument development		BNL-NSLS	DP Siddons 516-344-2738 516-344-5627	DP Siddons 516-344-2738 516-344-5627
X28A	Instrument development; Photon-based diagnostics and detector development		BNL-NSLS	P Stefan 516-344-2117	P Stefan 516-344-2117
X28B	Photon-based diagnostics and detector development		BNL-NSLS	P Stefan 516-344-2117	P Stefan 516-344-2117
X28C	Photon-based diagnostics and detector development		BNL-NSLS	P Stefan 516-344-2117	P Stefan 516-344-2117
X29A	(Unassigned)				
X29B	(Unassigned)				
X30	Diagnostic				

Beamline X7B: Time resolved powder diffraction patterns of thermal transformations in potassium nitrate obtained using the Translating Image Plate technique. [P. Norby and J.C. Hanson (BNL Chemistry Department), and A. Nørlund Christensen (University of Aarhus, Denmark)]

APPENDICES

ABSTRACTS & PUBLICATIONS

From the Editor

This year's Activity Report abstracts were entered by the authors via the Electronic Submission System (ESS). The ESS takes information entered through the Forms function on the World Wide Web and stores it in a database optimized for document handling. Composition routines then perform the integration of text and figures and output our choice of PostScript file (for the author to view and also to go to the printer), SGML file (Standardized Generalized Markup Language) for electronic publishing, and HTML (Hyper Text Markup Language) for dissemination on the World Wide Web. Furthermore, the ESS allows full storage and retrieval of the abstracts, sorted by beamline and author, and we expect that for next year it will be available electronically two to three months before the printed product is released.

Over 480 abstracts were received for this 1995 edition, which is about 10% more than last year when we also accepted paper submissions. We thank everyone who used the ESS, especially for the helpful feedback and suggestions. To access the completed abstracts as well as the ESS on the World Wide Web, select Open URL from the Mosaic File Menu, and enter <http://www.nsls.bnl.gov> to get to the NSLS Home Page. Choose Electronic Submissions; all instructions are provided in both viewable and downloadable format.

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Orientation of Ion Exchange Reacted Methylene Blue Molecules on Mica Investigated with NEXAFS

U1A

G. Hähner, A. Marti, and N. D. Spencer (Swiss Federal Institute of Technology, Zurich)

Layered silicates are of ever-increasing interest in colloid science, and their specific surface area is often a critical parameter. We have investigated the orientation and electronic structure of Methylene Blue ($C_{16}H_{18}N_3SH_3$) (MB) on mica, since it is often used to determine the specific surface areas of these high-surface-area materials. The molecule is generally considered to be a rectangular parallelepiped and to adsorb in a flat orientation. We have investigated the orientation and electronic structure of this system for several samples that were prepared by immersing the substrates for an extended period in aqueous solutions of MB of various concentration. The MB cations replace the K cations of the mica substrate by ion exchange.

Fig. 1 shows NEXAFS spectra recorded for different angles of incidence, Θ , at the C1s and N1s edges, recorded for a sample that was immersed for 14h in a 1mM MB solution. Both absorption edges exhibit a pronounced transition into unoccupied π^* orbitals that show a strong angular variation in intensity.

The difference between normal ($\Theta=90^\circ$) and grazing incidence ($\Theta=20^\circ$) is remarkable. From the observed angular variation, a tilt of the molecular plane relative to the surface normal of approximately 30° can be extracted. For lower concentrations of the solution we have found even smaller tilt angles. This result is in marked contrast to the flat orientation that is usually assumed and suggests that the specific surface areas determined with MB may, in general, be overestimated. In future experiments we will study further dye molecules that are also used to determine specific surface areas, in order to compare the results with those obtained for MB.

Figure 1. NEXAFS spectra of MB on mica recorded at the C1s and N1s edges. Both edges exhibit transitions into unoccupied π^* orbitals that show a strong angular variation in intensity.

Microspectroscopy characterization of III-V epi-layers for optoelectronics

U2B

G.L. Carr (Northrop Grumman ATDC)

Optoelectronic devices, such as vertical cavity surface emitting laser (VCSEL) diodes, are patterned from complex layers of III-V semiconductor compounds grown epitaxially on GaAs or other substrates. One VCSEL structure consists of two "mirrors" formed from GaAs/AlGaAs multilayer mirror stacks, above and below a quantum well structure that serves as the active medium. Fig. 1 indicates the overall device structure. Though intended for current bias operation, the device material can be tested by optical pumping with a focused laser. This can lead to microscopic damage near the focus spot, which can be investigated by IR microtransmission. The spectra for two sites are shown in Fig. 2. The transmission for an undamaged site shows a complex oscillatory behavior, consistent with interference due to multiple internal reflections between the top surface and various interfaces between layers. The oscillation period $\Delta\nu$ is related to the layer depth through $d = 1/(2n\Delta\nu)$ where n is the refractive index. Fourier analysis, combined with $n \approx 3.5$, allows the depth of the interfaces to be quantitatively determined. This is shown in Fig. 3. Note that the laser damaged area shows little evidence for layering, indicating that major structural damage has occurred. Since the sample can be scanned through the IR microspectrometer's focus, maps of layer depths and thicknesses can be extracted.

Figure 1. Epi-layer structure of a vertical cavity surface emitting laser.

Figure 2. Infrared microtransmission through damaged and undamaged VCSEL epi-layers.

Figure 3. Fourier analysis of interference pattern, indicating interface depths.

IR microspectroscopy study of Te precipitates in CdZnTe*

U2B

G.L. Carr and D.J. Larson, Jr. (Northrop Grumman ATDC)

CdZnTe (CZT) is a ternary II-VI semiconductor compound, used for both electronic and optical applications. The conditions for growing high quality CZT crystals often lead to the formation of tellurium precipitates a few microns in size. Infrared measurements of the precipitates (and the neighboring material) are useful for characterizing both the optical and electrical properties of the material.

We have performed a number of infrared microspectroscopy measurements on CdZnTe crystal wafers approximately 1 mm thick. One particular wafer had numerous internal Te precipitates. The precipitate size is typically 10 μm or less, which is beyond the capability of conventional-source IR microspectroscopy. However, using the IR microspectrometer at beamline U2B, we have achieved high quality spectra of individual, isolated precipitates. The transmission spectra of one such precipitate is shown in Fig. 1. At short wavelengths (less than 3 μm), the precipitate is opaque, while at longer wavelengths the transmission averages about 30%. This behavior is consistent with bulk tellurium, which is a semiconductor having an absorption onset at 2580 cm^{-1} (or 3.9 μm wavelength). The strong oscillations in transmission are attributed to multiple internal reflections within the precipitate, which behaves much like a confocal resonator for the focused IR from the microspectrometer.

The difference in transmission for Te at short and long wavelengths can be used to identify and locate the precipitates. Fig. 2 shows an IR absorbance map of a region of CZT containing two precipitates, which are apparent in the $\lambda = 2.5 \mu\text{m}$ absorbance map. At $\lambda = 6 \mu\text{m}$, the patches have nearly disappeared, consistent with tellurium.

*Portions of this work supported by NASA through contract NAS8-38147 and also by IR&D funds as part of a CRADA with Brookhaven National Laboratory.

Figure 1. Infrared transmission of a single tellurium precipitate buried within a CdZnTe wafer. The dashed line indicates the onset of absorption in bulk Te.

Figure 2. Infrared absorbance maps for a CdZnTe wafer region containing two Te precipitates. The two wavelengths shown span the absorption onset of Te, providing chemical contrast.

Infrared Microspectroscopy of Oil Inclusions in Quartz and Fluorite Matrices

U2B

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We have performed infrared microspectroscopy measurements using a 3x3 micron aperture on the Spectra-Tech IRus microspectrometer at U2B. We have mapped small fluid inclusions in fluorite from Tunisia and in quartz from a North-Sea core-drill. An example of a fluid inclusion from a sample from Tunisia is shown at left. This inclusion contains oil and CO₂. However, depending on the pressure and temperature conditions during the entrapment process, the proportion of CO₂ either dissolved in the oil, and/or in the gaseous phase in equilibrium with the oil can be drastically different. In Fig. 2 (top) we show a CO₂ map derived from the intensities of the 2335 cm^{-1} absorption band, corresponding to the C-O stretch mode. In Fig. 2 (bottom) we show a map of the intensities of the 2850 cm^{-1} band corresponding to C-H stretch vibrations.

We clearly see that the CO₂ in this inclusion is in the gas phase, well separated from the oil. The absorption magnitudes of the two components, the CO₂ and oil, indicate the relative thickness of the fluid inclusion. This opens up the possibility of performing a quantitative analysis on these very small inclusions.

Figure 1.

Figure 2.

IR TRANSMISSION STUDIES ON KC₆₀ SINGLE CRYSTALS *

U2B

L. Mihaly (SUNY @ Stony Brook), S. Pekker (RISSP, Budapest), L. Forro (EPFL, Lausanne), and G.L. Carr (Northrop Grumman ATDC)

The fullerene molecules in the alkali fulleride KC₆₀ form polymeric chains[1]. Earlier ESR and IR studies indicated that the polymer is metallic, and, in contrast to other alkali fullerides, this material is stable in air[2]. Up to now, nearly all of the investigations on this compound were performed on polycrystalline samples, since the individual crystallites were too small for most of the measurement techniques. The IR microscope at U2B provided a unique opportunity to explore the properties of a single crystal of this compound. The goal of the present investigation was twofold: To establish that the bulk of the single crystal is indeed made of KC₆₀ and to explore if there is any evidence for optical anisotropy, as expected from the crystal structure. The samples for this study were produced by co-evaporation of potassium and C₆₀ and subsequently treated in toluene. The sample preparation is discussed in detail in Ref. [3]. The typical dimensions of a single crystal ("fiber") were 0.5mm × 10μm × 0.05μm.

The optical samples were made by placing a drop of toluene with dispersed fibers onto a KBr disk. The IR beam was focused to a 6μm by 6μm spot onto one of the fibers. Fig. 1 shows the optical spectrum. The characteristic vibrational modes of KC₆₀ are clearly visible, confirming the composition of the sample. The measurement has been repeated on several crystals and the results were similar.

A wire grid polarizer was used to study the polarization dependence of the spectra. Unexpectedly, neither the vibrational peaks, nor the broad band optical absorption were found to depend on the direction of the polarization. Subsequent electron microscopy studies revealed that the fibers are in fact *twinned* single crystals [4]. The twinning occurs on a length scale of about 1μm, and averaging over several domains explains the absence of the anisotropy in the present IR study.

- [1] P. W. Stephens *et al.*, Nature, 370, 636 (1994).
- [2] D. Koller *et al.*, J. Appl. Phys. 66, 1015 (1995).
- [3] S. Pekker *et al.*, Science, 265, 1077 (1994).
- [4] M. Carrard *et al.*, submitted to Synthetic Metals.

Figure 1. IR transmission spectrum measured on a single fiber of KC₆₀. The beam is perpendicular to the fiber and the transmission does not depend on the direction of polarization.

Localization of Infrared Sampling in Human Hair.

U2B

David L. Wetzel (Kansas State Univ.)

Localization of drugs in human hair has been one of the difficult goals of forensic science. One approach involves the use of IR spectroscopy to detect the vibrational modes that can uniquely identify a given organic compound. Infrared microspectroscopy studies of longitudinally microtomed, single hairs embedded in paraffin have been conducted by K. Kalisinski (Armed Forces Pathology Research Laboratory). For these specimens, 20 X 100 μm sampling apertures were used to obtain sufficient signal through a typically 6 μm thick section. This aperture was stepped in 5 μm increments across the specimen producing a profile of the drug deposition or protein concentration across the hair. A higher spatial resolution is desirable, since human head hair grows approximately 1 cm per month, or about 13 μm an hour. If a dose of cocaine is metabolized in approximately 15 minutes, then the deposition of the dose would be localized to a 3 μm segment of hair.

Using IR synchrotron radiation in combination with the FT-IR microspectrometer at U2B, we can improve the spatial sensitivity considerably. Sampling apertures of 5 μm or less, corresponding to a hair growth time of 22 minutes, are feasible. In addition to temporal sensitivity, the spatial resolution of the U2B microscope also enhances the chemical sensitivity, since the 3 μm segment of hair represents a larger fraction of the microspectrometer's sensing region, when compared to a more conventional 20 X 100 μm aperture. There remain sample preparation issues, such as microtoming appropriately thin and flat specimens compatible with the small IR sampling area.

* This work has been supported by NSF grants INT-9414840 and DMR-9501325 and US-Hungarian Joint fund No. 225 and OTKA T4222.

Alkali Adsorption on $K_{0.3}MoO_3$

Klaus Breuer, Cristian Stagarescu, Kevin E. Smith (Boston University), Martha Greenblatt, William McCarroll (Rutgers University)

The blue bronze $K_{0.3}MoO_3$ is a layered solid that exhibits all the characteristic properties of a quasi-one dimensional (1D) conductor, including the occurrence of a Peierls transition to a charge density wave (CDW) state at 180 K. Recently, photoemission experiments from this oxide have received a lot of attention, as it has been claimed that the observation of a low emission intensity at the Fermi level (E_F) and the absence of a Fermi edge in angle integrated photoemission are indication of a Luttinger ground state of the 1D electron system.¹ However, it is controversial, as whether the surface electronic structure, as it is measured by photoemission, is representative of the bulk.²

In a recent study we have investigated how the electronic surface structure is affected by modifications of the alkali concentration on the surface. Variations in the alkali content are believed to be responsible for the observed variations in the emission from the $Mo\ 4d$ states and in the work function that we observed for different cleaves (cleavage occurs along planes of alkali atoms). In order to systematically study this dependence we evaporated Cs onto $K_{0.3}MoO_3$ surfaces and used angle resolved photoemission (ARP) to measure the modifications of the electronic surface structure.

As can be seen in Fig. 1, the adsorption of sub-monolayer quantities of Cs leads to strong variations in the $Mo\ 4d$ emission, and in particular to a shift away from E_F This is caused by charge transfer from the highly electropositive Cs to the substrate and a filling of $Mo\ 4d$ states. The variations in the $Mo\ 4d$ photoemission line shape upon band filling can be explained by conventional quasiparticle theories and do not indicate a Luttinger ground state.

[1] B. Dardel, D. Malterre, M. Grioni, P. Weibel, Y. Baer and F. Levy, Phys. Rev. Lett. 67, 3144 (1992).

[2] K. Breuer, K. E. Smith, M. Greenblatt and W. McCarroll, J. Vac. Sci. Technol. A12, 2196 (1994).

Figure 1. Normal Emission ARP spectra from a cleaved $K_{0.3}MoO_3$ surface (a) and with sub-monolayer overlayers (b,c).

Electronic Structure of the Quasi-Two Dimensional Conductor $Na_{0.9}Mo_6O_{17}$

Klaus Breuer, Cristian Stagarescu, Kevin E. Smith (Boston University), Martha Greenblatt and Kandalam Ramamunujachary (Rutgers University)

The purple bronze $Na_{0.9}Mo_6O_{17}$ is a quasi-two dimensional (2D) conductor that undergoes a metal-metal transition to a charge density wave state at 80 K.¹ CDW instabilities are most commonly observed in quasi-one dimensional (1D) systems and are caused by the strong nesting of 1D Fermi surfaces. In order to explain the observed instabilities in 2D systems, Whangbo et al. introduced the concept of hidden Fermi surface nesting.² According to this model, the 2D Fermi surface can be viewed as a combination of 1D Fermi surfaces, with distinct quasi-1D nesting vectors.

In order to verify this concept we used angle resolved photoemission (ARP) to measure the Fermi surface of this oxide. Fig. 1 shows a series of ARP spectra from cleaved $Na_{0.9}Mo_6O_{17}$. Within 1 eV of the Fermi level three clearly dispersing bands are observed. Fermi level crossings of two different bands are observed and lead to electron and hole pocket structures in the Fermi surface. The features of the measured Fermi surface are in agreement with the calculations of Whangbo, and thus support the concept of hidden Fermi surface nesting.

1. M. Greenblatt, Chem. Rev. 88, 31 (1988).

2. M.-H. Whangbo, E. Canadell, P. Fourty and J.-P. Pouget, Science 252, 96 (1991).

Figure 1. Series of ARP spectra from cleaved $Na_{0.9}Mo_6O_{17}$

E. Goering, M. Klemm, S. Horn (U. Augsburg, Germany), and M. L. denBoer (Hunter CUNY)

During our measurement time in 1995 June we obtained photoemission spectra of single crystalline V_2O_3 , VO_2 , and MoO_2 in the photon energy range 25 to 100 eV. Measurements were taken above and below the temperature T_{MI} at which a metal-insulator (MI) transition occurs in V_2O_3 and VO_2 . From fits of the Fermi energy cut off we estimate the energy resolution of the measurements to be 150 meV, determined largely by the analyser. Since the crystals have less than cubic symmetry below the MI transition, spectra were taken for various orientations of the polarisation vector relative to the crystal axes.

Fig. 1 shows spectra taken for VO_2 at different incident energies above and below the transition. The various resolved features show dispersion which is particularly strong far from the Fermi energy E_F but only weak for the features close to E_F . These features exhibit a prominent resonance, having maximum intensity at ≈ 60 eV, which is typical for V 3d states. (This effect is not evident in Figs. 1 and 2, in which spectra are normalized to their respective intensity maxima in order to show the dispersion.)

At all incident energies, a Fermi cut off is observed. The width of the peaks fitted to the spectrum is larger than the energy resolution, implying that the intrinsic combined electron-hole lifetime is short. We now consider the differences between spectra of "warm" (conducting) and "cold" (insulating) samples. When the sample is cooled below T_{MI} , the main effect seen in Fig. 1 is that the intensity at E_F vanishes, suggesting the opening of a gap at the MI transition, which has been previously observed. Correspondingly, there is a slight increase in intensity just below E_F . On the other hand, at a different orientation of the sample, as shown in Fig. 2, the spectral changes at the MI transition are much more dramatic. We again see the opening of a gap, as expected. However, there is also a considerable increase in the intensity of the features just below E_F , especially in the vicinity of the resonance at ≈ 60 eV photon energy. Using this information, we can in principle determine the orientation, and hence the angular momentum character, of precisely those electronic states which are most involved in the metal-insulator transition.

Similar measurements have been performed for V_2O_3 and MoO_2 . For these materials as well we observe only weak dispersion for features close to E_F . For V_2O_3 the opening of a gap below T_{MI} is suggested.

The orientation dependence of the MoO_2 spectra is especially interesting in comparison with that of the isostructural compound VO_2 .

Figure 1. VO_2

Figure 2. VO_2

L.R. Masliah, R.G. Jordan and S.L. Qiu (Florida Atlantic University)

We have begun making a detailed study of the electronic structure in CuAu using a combination of experimental photoemission measurements and first principles calculations. Alongside we show some photoemission measurements obtained for the (111) surface at normal emission; the states that are being probed lie along the Λ direction in the Brillouin zone. In addition to a number of "bulk" features we can also identify at least two surface states; there is a Shockley-type state at about 0.5 eV binding energy and a state at about 7.5 eV that lies in the s-d gap very close to the band edge at the $\bar{\Gamma}$ -point.

We are currently carrying out electronic structure calculations for the (111) surface using a slab geometry. We will use the layer potential functions that are generated in first-principles photocurrent calculations for direct comparison with our photoemission measurements. (This work is being carried out in collaboration with Dr. B. Ginatempo, University of Messina.) **Acknowledgments:** We thank Dr. M.L. Shek for her help, guidance and patience.

Figure 1. Photoemission spectra from CuAu(111) at normal emission. The photon energy is stepped in increments of 5 eV from 25 eV (bottom) to 70 eV (top). The incidence angle is 60° .

* This work was supported by a grant from NSF: DMR-9120120

Electronic Structure of the Organic Conductor κ -(BEDT-TTF) ₂ Cu[N(CN) ₂]Br	U4A
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C. Stagescu, K. Breuer, K. E. Smith, *Department of Physics, Boston University*, R. Haddon, *AT&T Bell Labs*, J. S. Brooks, *Department of Physics, Florida State University*

The organic conductor κ -(BEDT-TTF)₂Cu[N(CN)₂]Br is a layered quasi-two dimensional material that is derived from the donor molecule BEDT-TTF. These charge transfer salts have received considerable interest, due to the occurrence of transitions to either a superconducting state or to a density wave phase below a critical temperature.

We have studied the electronic structure of this organic conductor using angle-resolved photoemission. Fig. 1 shows a typical spectrum, taken with 24 eV photons on a sample cleaved *in situ*. In general agreement with an earlier study of Liu *et al.* we do not observe significant emission intensity at the Fermi level (E_F).¹ An interpretation of these results requires knowledge of the surface properties of this material. (These have not been studied up to date). Single crystals of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br are expected to cleave exposing the conducting layers. As the separation between these layers is larger than the escape depth of the photoelectrons, photoemission only probes the top layer of the sample. Only when the surface's stoichiometry is representative for the bulk, the observation of a low emission intensity at E_F can be related to the electronic bulk structure of this conductor. It is therefore planned to systematically study the surface properties of these materials. In addition the electronic structure will be studied with X-ray emission spectroscopy, as this technique is not surface sensitive as photoelectron spectroscopy.

Work supported in part by NSF CAREER AWARD DMR 95-01174.

1. R. Liu *et al.* Phys. Rev. B51, 6155 (1995).

Figure 1. Normal emission ARP spectrum from κ -(BEDT-TTF)₂Cu[N(CN)₂]Br

Surface states on the (100) and (001) surfaces of equi-atomic CuAu *	U4A
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Xumou Xu, R.G. Jordan and S.L. Qiu (Florida Atlantic University).

We are making a detailed experimental and theoretical investigation of surface states on the (100) and (001) surfaces of CuAu (L1₀, layered tetragonal structure with $c/a = 0.925$). We have identified Tamm-type surface states on both the (100) and (001) surfaces, labelled S1 and S2 on the accompanying figure for the (100) surface, located near the $\bar{M}$ -point, and a Shockley-type state near the $\bar{X}$ -point in the binding energy range 0-1eV on the (100) surface. By making a careful analysis of the dispersion of S1 and S2 on the two surfaces we have determined the surface lattice constants and we conclude that the (100) surface is not reconstructed. Preliminary calculations of the electronic structure at the CuAu(001) surface using a slab geometry, with an Au termination, shows the appearance of these Tamm-type states. More detailed calculations are underway. (This work is being carried out in collaboration with Dr. G.Y. Guo, Daresbury Laboratory.) Acknowledgments: We thank Dr. M.L. Shek for her help and advice.

Figure 1. Photoemission spectra from the (100) surface of equi-atomic CuAu at various emission angles in the (001) mirror plane. The photon energy is 25eV with an incidence angle of 60°.

* This work is supported by a NSF grant: DMR-9120120

Determination of Helicity-Dependent Absolute PhotoAbsorption Cross Sections at the L-edges of Fe, Co, and Ni *

U4B

V. Chakarian and Y.U. Idzerda (NRL), J.-H. Park, G. Meigs, and C.T. Chen (AT&T)

The knowledge of absolute X-ray photoabsorption cross sections is a prerequisite in many experiments that employ photons as a probe. In this article, we present a method which enables the determination of the absolute photoabsorption cross sections in the soft X-ray region. Absorption spectra are obtained in transmission by using a photodiode mounted behind the samples which consist of a ~ 50 Å thin film evaporated in situ onto $\sim 1\mu\text{m}$ thick semi-transparent parylene, $(\text{C}_8\text{H}_8)_n$, substrate [1]. The measurements, made by employing circular polarized photons, enable the determination of μ_+ and μ_- corresponding to the absorption cross sections of left- and right-circular polarized photons (or photon spin parallel and antiparallel to the sample magnetization direction), respectively. The total photoabsorption cross section can also be obtained by using $\mu_{\text{Tot}} = (\mu_+ + \mu_- + \mu_0)/3$, where $\mu_0 = (\mu_+ + \mu_-)/2$ is the photoabsorption cross section for linear polarized photons (not helicity dependent). As an example, the figure below shows the corresponding cross sections per Fe atom, expressed in cm^{-1} . The spectra were scaled to calculated absorption cross sections [2] in the pre- and post-edge regions and the atomic density in the film was assumed to be same as the bulk value. An independent confirmation of the resulting μ_{Tot} was obtained by correlating the absorption strength at the L_3 peak with ex-situ X-ray fluorescence measurements from a series of samples with different thicknesses. The two methods yield values that are very similar. The results for ferromagnetic Fe, Co, and Ni and as well as other non-ferromagnetic 3d elements will be presented in an upcoming publication. Note that in the case of a non-ferromagnetic material, all three curves shown in the figure would be identical.

[1] C.T. Chen et. al., NSLS Activity Report, p. A-25 (1994).

[2] J.J. Yeh and I. Lindau, Atomic Data and Nuclear Data Tables, 32, 1 (1985).

Figure 1.

* VC Supported by ONR.

Element-Specific Orbital and Spin Moments of Transition Metal Alloys via MCD *

U4B

V. Chakarian and Y.U. Idzerda (NRL), J.-H. Park, G. Meigs, and C.T. Chen (AT&T)

Magnetic circular dichroism (MCD), in conjunction with the recently developed sum-rules, can be used to decompose the total magnetic moment of a magnetic material into the orbital and spin moment contributions. In this article, we extend the use of the MCD method to transition metal alloy systems $\text{Fe}_x\text{Co}_{1-x}$ and $\text{Co}_x\text{Ni}_{1-x}$. XAS spectra are obtained in transmission by using a photodiode mounted behind the samples which consisted of a thin film evaporated in situ onto semi-transparent parylene substrates. The data reduction process is discussed in detail elsewhere [1]. As an example, the MCD spectrum (solid) from a thin film $\text{Fe}_{48}\text{Co}_{52}$ alloy and its integral (dashed) are shown in Fig. 1, where p and q are the integrated MCD intensities over the L_3 and L_3+L_2 edges, respectively. Using these values, it is possible to directly obtain the ratio of orbital to spin moments, m_l/m_s , of each element. The measurements were repeated for a large number of alloy films spanning the entire Fe-Co-Ni phase diagram, and the results are shown in Fig. 2 along with Einstein-de Haas gyromagnetic ratio data [2] and theoretical predictions [3]. The preliminary results thus far indicate that the orbital and spin moments for each of these elements do not vary significantly, within experimental uncertainty, away from their elemental values. This is in contradiction to the theoretically expected non-monotonic behavior of the orbital moment. The discrepancies may be, in part, due to the fact that the films used in the present work were random alloys. The results of this study will be presented in more detail in upcoming publications.

[1] C.T. Chen et. al., Phys. Rev. Lett., 75, 152 (1995).

[2] K. Adachi et. al., Magnetic Properties of Metals, Vol. III/19a, p. 178 (Springer-Verlag, Berlin, 1986).

[3] P. Sderlind, et. al., Phys. Rev. B, 45, 12911 (1992).

Figure 1.

* VC Supported by ONR.

Figure 2.

Giant magnetic effects in the L-edge extended X-ray absorption fine structure of 3d transition metals *

U4B

Y.U. Idzerda, V. Chakarian, and K. Kemner (NRL), J.-H. Park, G. Meigs, and C.T. Chen (AT&T)

Transmission MCD measurements extended to the EXAFS region have been performed for Fe, Co, and Ni thin films grown under ultra-high vacuum conditions by e-beam evaporation from pure metal sources onto $\sim 1\mu\text{m}$ thick semi-transparent parylene substrates. Helicity dependent soft X-ray absorption spectra (XAS) were obtained by measuring the relative photon flux transmitted through the magnetic thin films using a photodiode mounted behind the sample. The photon beam was incident at 45° with respect to the sample normal with the energy resolution and the degree of circular polarization set at $\Delta E \sim 0.5\text{ eV}$ and $p_c = 0.75$, respectively. The MCD data were measured by alternating the magnetization at each photon energy. The EXAFS and magnetic EXAFS (MEXAFS) measurements for the L-edges of 3d transition metals are shown at right. The leftmost panel of the figure shows the Fe XAS spectrum in which the vertical scale in the EXAFS region is expanded. The next panel shows the Fe MCD signal, where the vertical scale has been expanded.

The results of similar measurements at the L-edge of Co and Ni thin films grown similarly are shown in the remaining panels. The XAS spectra display large EXAFS oscillations indicating reasonable crystalline quality of the films. There is a substantial difference in the detailed shape of the EXAFS oscillations between Fe, Co, and Ni due to the differences in the local atomic structure of these films and to the changes in the interference between the oscillations associated with the two edges. Note that although the EXAFS oscillations of the Fe, Co, and Ni films are of comparable intensity, the relative amplitude of the MEXAFS compared to the EXAFS changes dramatically from $\pm 5\%$ for Fe, $\pm 2.5\%$ for Co, to $<\pm 0.5\%$ for Ni of the respective EXAFS oscillations. Noting that the spin moments of bcc Fe, hcp Co, and fcc Ni are 2.1 , 1.5 , and $0.6\mu_B$, respectively, these measurements indicate that the size of the effect does not scale linearly with the spin moment of the scattering atom.

Figure 1.

* VC Supported by ONR.

Magnetic Field Dependence of Mn Moment in FeCo/Mn/FeCo Trilayers *

U4B

Y.U. Idzerda, V. Chakarian, G.A. Prinz (NRL), C. Gutierrez (S.W. Texas Univ.), H.J. Lin, G. Meigs, and C.T. Chen (AT&T)

Recently a new multilayer system, essentially bcc Co/Mn/Co (the actual composition of the trilayer is $\text{Fe}_{25}\text{Co}_{75}/\text{Mn}/\text{Fe}_{25}\text{Co}_{75}$), has been found to have quite a unique coupling behavior. Instead of simply exhibiting aligned or anti-aligned configuration of the two ferromagnetic films, the magnetic moments of the two single-crystal FeCo alloy layers are strongly coupled at a fixed angle with respect to one another. Because this coupling angle is dependent on the thickness of the Mn layer, this unique coupling must be reflected in an atypical magnetic structure of the embedded Mn layer. The magnetic multilayer consists of two $100\text{ \AA}$, single-crystal $\text{Fe}_{25}\text{Co}_{75}$ alloy films, separated by a thin 4.5 monolayer ($8.7\text{ \AA}$) Mn interlayer. The trilayer was grown on a thick $\sim 660\text{ \AA}$ ZnSe(001) buffer layer and capped with a $30\text{ \AA}$ Al film to prevent oxidation. The element-specific magnetic hysteresis curves were determined by monitoring the partial X-ray fluorescence yield, as a function of the applied magnetic field, at the L_3 edges of the relevant elements. The seemingly complicated Mn hysteresis loops are the result of a nearly-rigid 23° rotation of the average Mn moment with respect to the average Fe moment. The rotation angle, however, is not completely field independent. The magnetic field dependence of the canting angle is shown in the figure below. The angle varies from 30° at low fields to only 20° at high fields. The 23° rotation and this field dependence behavior is inconsistent with an interdiffusion of the Mn into the FeCo alloy layers.

Figure 1.

* VC Supported by ONR.

Electronic aspect of ferromagnetic transitions in $\text{La}_{1-x}(\text{Ca}, \text{Pb})_x\text{MnO}_3$	U4B
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J.-H. Park, C. T. Chen, S.-W. Cheong, W. Bao, G. Meigs, (AT&T Bell Labs), V. Chakarian, and Y. U. Idzerda (NRL)

U4B $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A} = \text{Ba}, \text{Sr}, \text{Ca}, \text{Pb}, \text{etc.}$) exhibits an intriguing ferromagnetic transition accompanied by a large change in resistivity. To investigate electronic change through the transition, we have measured high resolution valence band photoemission spectra and resonant photoemission spectra of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ($T_C \approx 260\text{K}$) and $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ ($T_C \approx 330\text{K}$) for different temperatures. The high resolution spectra and Mn 2p edge on-resonance spectra shown in the figure were taken with the experimental resolution of 60 meV and of 600 meV, respectively. As shown in Fig. (a), the high resolution wide scan spectra exhibits nearly no difference for the different temperatures except for a variation near the Fermi level. The magnified near E_F spectra are shown in Fig. (b). For $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, no density of states at E_F , $n(E_F)$, is observed at 280 K ($> T_C$), but $n(E_F)$ increases upon cooling below T_C and a metallic Fermi edge is clearly observed at 80K. Similar temperature-dependence of $n(E_F)$ was also observed in $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$. The Mn 2p edge on-resonance spectra, in which the Mn 3d emission is enhanced exclusively, are shown in Fig. (c). Upon cooling from the high to low temperature, an energy shift of $\sim 0.2\text{eV}$ ($\sim 0.25\text{eV}$) to low energy binding energy is observed for the lowest binding energy state, which corresponds to the $^4\text{A}_2$ final state, of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ($\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$).

The data clearly show that the band gap collapses below the Curie temperature and the density of states at E_F increases with cooling, providing a conclusive microscopic evidence for an insulator-metal transition near T_C . Our study, furthermore, shows that the fascinating paramagnetic insulator to ferromagnetic metal transition results from the close interplay between the charge fluctuation energy for an electron hopping from Mn^{3+} to Mn^{4+} sites, and spin-dependent electron hopping energy.

$\text{Mn}^{3+}\text{-Mn}^{4+}$ mixed valence driven by Co doping in LaMnO_3	U4B
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J.-H. Park, S.-W. Cheong, C. T. Chen (AT&T Bell Labs.), V. Chakarian, and Y. U. Idzerda (NRL)

LaMnO_3 is an antiferromagnetic insulator with Mn^{3+} . Substitution of La sites with alkaline earth elements, i.e. $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A} = \text{Sr}, \text{Ca}, \text{etc.}$), induces Mn^{4+} and the system becomes $\text{Mn}^{3+}\text{-Mn}^{4+}$ mixed valent. Then the system exhibits an intriguing ferromagnetic transition, which arises 'colossal' magnetoresistance. It has also been found that the transition temperature as well as the magnetoresistance varies as a function of the lattice constant. Hence it is interesting to study $\text{La}(\text{Mn}_{1-x}\text{Co}_x)\text{O}_3$ system, in which the lattice constant also changes as a function of x .

We have investigated $\text{La}(\text{Mn}_{1-x}\text{Co}_x)\text{O}_3$ by using x-ray absorption and resonant photoemission spectroscopies. Fig. (a) shows Co $L_{2,3}$ edge x-ray absorption spectra of $\text{LaMn}_{0.85}\text{Co}_{0.15}\text{O}_3$ in comparison with those of LaCoO_3 (Co^{3+}) and CoO (Co^{2+}). As can be seen in the figure, the spectrum of $\text{LaMn}_{0.85}\text{Co}_{0.15}\text{O}_3$, surprisingly, exhibits almost identical features in both L_2 and L_3 regions to those of CoO but completely different from those of LaCoO_3 , showing that Co in LaMnO_3 is not trivalent but divalent. These results indicate that Co doping creates $\text{Co}^{2+}\text{-Mn}^{4+}$ pairing and induces the $\text{Mn}^{3+}\text{-Mn}^{4+}$ mixed valent system as in $\text{La}_{1-x}\text{A}_x\text{MnO}_3$. Fig. (b) shows Co 2p edge on- and off-resonance photoemission spectra of $\text{LaMn}_{0.85}\text{Co}_{0.15}\text{O}_3$, which were taken with 778.5eV and 775eV photon energies, respectively. In the on-resonance, the spectrum in the valence band region is completely dominated by Co 3d emission due to a giant resonance enhancement. As can be in the difference spectrum shown in the bottom, the Co 3d lowest bonding energy states, which correspond to $^5\text{T}_2$ and $^3\text{T}_1$, locate $\approx 0.7\text{eV}$ higher binding energy than the Mn 3d lowest binding energy state, which corresponds to $^4\text{A}_2$.

The data show that Co doping in LaMnO_3 changes the system to be $\text{Mn}^{3+}\text{-Mn}^{4+}$ mixed valent, not only the lattice constant.

Figure 1.

Figure 2.

A Study of Ethanol Adsorption on Si(100) Surfaces Using Mid-to Far-Infrared Spectroscopy

U4IR

J. Eng, Jr., L.M. Struck, B.E. Bent, G.W. Flynn, (Columbia University), Y.J. Chabal, K. Raghavachari (AT&T Bell Laboratories), G.P. Williams (BNL-NSLS)

There has been considerable commercial interest [1] in the use of tetraethoxysilane (TEOS) as a silicon source for chemical vapor deposition processes related to SiO₂ growth. In turn, this interest has motivated studies of ethanol adsorption on Si(100) surfaces, since it has been shown [2] that ethanol decomposes upon adsorption to form a bound ethoxy group which, through infrared (IR) spectroscopy, has been determined to resemble the ethoxy groups in adsorbed TEOS. Though these IR Studies has been quite fruitful, they have also been limited by strong silicon phonon absorptions to frequencies above 1300 cm⁻¹.

In the studies described here, the adsorption of ethanol on clean Si(100) surfaces, has been investigated using a specially prepared cobalt implanted silicon sample as described in more detail in the companion summary about water adsorption on Si(100) found elsewhere in this Annual Review. The adsorption of three isotopes of ethanol (-d₀, -d₃, -d₆) have been studied, and shown in the figure are the infrared spectra corresponding to approximately monolayer coverage of each isotope on clean Si(100). These spectra represent the first time that the skeletal modes of bound ethoxy groups have been observed on silicon surfaces, and show that the ethanol dissociatively adsorbs across the Si(100) dimer to yield a bound ethoxy group on one side and an adsorbed hydrogen on the other. Furthermore, the surface dipole selection rule, which results from the buried metallic layer, indicates that the ethoxy group is adsorbed such that the C_{3v} axis of the methyl group is perpendicular to the surface, quite different from the bonding geometry for ethanol adsorption onto metals. Normal obtained by *ab-initio* methods have been successful in assigning all the major features in the ethanol-d₀ spectrum and more calculations are underway to assign the features for the ethanol -d₃ and -d₆ spectra.

[1] L. Tedder, G. Lu, and J. Crowell, *J. Appl. Phys.*, 1991, 69(10) 7037-49

[2] J. Crowell, L. Tedder, H. Cho, F. Cascarano, and M. Logan, JVST A 8(3) 1864-70

Study of Water Adsorption on a Si(100) Surface Using Far-Infrared Spectroscopy

U4IR

J. Eng, Jr., L.M. Struck, B.E. Bent, G.W. Flynn (Columbia University), Y.J. Chabal, K. Raghavachari (AT&T Bell Laboratories), G.P. Williams (BNL-NSLS)

Understanding the bonding geometry and dynamics in the adsorption of water on Si(100) surfaces is technologically important for device manufacture. Infrared (IR) spectroscopy is, in general, useful for studying bonding geometries and dynamics. For silicon, however, external reflection IR spectroscopy has poor signal to noise, while transmission IR spectroscopy is limited by phonon absorptions below ~1400 cm⁻¹ so that only high frequency vibrations such as those involving hydrogen can be observed.

In the studies described here, specially prepared Co⁺ implanted Si(100) wafers are used to overcome the problems mentioned above. After Co⁺ implanted each wafer is annealed at 1000°C, which causes the subsurface cobalt to form an abrupt, semi-metallic, reflective COSi₂ layer which is located 50 nm below the surface and is 50 nm thick. The annealing step also repairs the Si overlayer damaged during implantation, so that an ordered Si(100) 2x1 surface is obtained. In this type of sample, the silicon overlayer is optically thin, so that phonon absorptions do not dominate, yet chemically thick enough to exhibit the same surface chemistry as Si(100) wafers with no implantation.

Using these Co⁺ implanted samples, we have been able to perform spectroscopic studies in the far infrared for H₂¹⁶O, H₂¹⁸O and D₂¹⁶O adsorption onto Si(100) surfaces. The spectra for H₂¹⁶O and D₂O (shown below) indicate that water dissociatively adsorbs across the Si(100) surface dimer. Importantly, use of the cobalt implanted sample, along with the intense synchrotron light, has enabled us to see a weak mode at 896 cm⁻¹ in the H₂¹⁶O spectrum, which had not been previously observed. Normal mode calculations show that for H₂¹⁶O the Si-OH stretching mode and the Si-O-H bending mode are sufficiently close in energy to couple mechanically and split apart, resulting in a mode at 825 cm⁻¹ and at 896 cm⁻¹. Thus, we have been able to resolve the puzzling isotope shift seen previously by electron energy loss spectroscopy (EELS) [1]. The features in the H₂¹⁸O and D₂¹⁶O spectra have also been assigned, based on the calculations.

[1] H. Ibach, et al., Solid State Communications, Vol. 42 No. 6, p457.

c Axis Response of La_2CuO_4 studied by Far IR Ellipsometry *
U4IR

R. Henn, J. Kircher, and M. Cardona (Max-Planck Institut FKF, D-70569 Stuttgart, Germany), and G.P. Williams (BNL-NSLS)

In order to investigate far infrared properties of superconducting cuprates we coupled a rotating analyzer ellipsometer to the Fourier spectrometer of the U4IR beamline. The "in plane" dielectric function in the far IR of these materials is dominated by the electronic response in accordance with the picture of charge carriers having a high mobility within the CuO_2 planes. Much more unsettled is the picture of charge transport perpendicular to the CuO_2 planes, where usually a much lower conductivity is observed. We have measured the complex dielectric function of La_2CuO_4 ($T_c \approx 33\text{K}$) for c polarization at different temperatures. The real (ϵ_1) and imaginary (ϵ_2) part of the dielectric function measured at 300 K are shown in the figure to the left. The spectra are dominated by the phononic response of the sample. In agreement with the low conductivity along this direction, we only observe a weak, almost temperature independent "background" attributed to free carriers. We can fit (solid lines) our data (dots) with a Drude term ($\omega_p \approx 830\text{cm}^{-1}$, $\Gamma \approx 440\text{cm}^{-1}$) accounting for the electronic response and 3 Lorentzians representing the 3 strongest phonons (at 235, 354, and 500 cm^{-1}). The oscillator strength of the mode appearing at 31 cm^{-1} is too weak to obtain a satisfactory fit. As an example we show on the right hand side the temperature dependence of the parameters (oscillator strength S , energy E , and full width at half maximum Γ) for the 235 cm^{-1} mode. The preliminary analysis of the data presented here gives no indication for phonon anomalies at T_c and no sign of superconductivity in the electronic response of La_2CuO_4 for c polarization.

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FIR-Synchrotron Study of CO_2 Activation and Alkali Compound Formation on $\text{Cu}(111)$ *
U4IR

F.M. Hoffmann (Exxon Research and Engineering), J. Paul (Physics III, Royal Institute of Technology, Stockholm, Sweden), and G.P. Williams (BNL-NSLS)

Alkali metals are frequently used as catalytic promoters for the activation of CO_2 , e.g. in the methanol synthesis reaction. Recent studies of this reaction at high pressure have shown the importance of alkali compound formation in this reaction. Vibrational spectroscopy offers in principle an excellent fingerprint of the different compounds formed by the reaction of CO_2 with alkali metals. However, the actual vibrational spectra observed after reaction of CO_2 with potassium layers reveal an extraordinary complexity due to the presence of a mixture of different species and coordinations, i.e. CO_2 , CO_2^- , CO_2^{2-} , $\text{C}_2\text{O}_4^{2-}$, and CO_3^{2-} . In order to characterize the individual species, we have synthesized thin films of CO_2 , oxalate, and carbonate species by coevaporation of potassium and CO_2 . The reflectance changes induced IR, we obtain a complete set of high resolution vibrational spectra of these species from the Mid to Far-IR. The latter region is of particular importance since it contains information about the K-O bond formation and hence the molecular coordination. Isotopic substitution and the comparison with theoretical calculations allow the determination of molecular identity, symmetry, force constants, and bond angles. Finally the thermal decomposition pathways of the various compounds and the relationship between IRAS/TDMS.

[1] F.M. Hoffmann, M.D. Weisel and J. Paul, Surf. Sci. 316, 277 (1994).

Figure 1.

* The NSLS is supported by the US DOE under contract DE-AC02-76CH00016.

Infrared Spectroscopic Study of Water Adsorption on Ni(110)

U4IR

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The adsorption of water on Ni(110) at 180 and 230 K has been studied by Fourier Transform Infrared Reflection-Absorption Spectroscopy in the 250-2000 cm^{-1} frequency range using synchrotron radiation. Based on the previous study [1], water does not dissociate on Ni(110) at 180 K. However, it partially dissociates and desorbs above 200 K.

We have observed two broad vibrational bands at 670 and 800 cm^{-1} with peak widths (FWHM) of 40-60 cm^{-1} for the saturated $\text{H}_2\text{O}/\text{Ni}(110)$ surface at 180 K. Furthermore, upon heating the surface to 230 K, we have observed a frequency shift of these two vibrational bands to 780 and 950 cm^{-1} as well as a narrowing of the FWHM to 15 and 24 cm^{-1} , respectively. In the isotopic experiment using D_2O , we have measured two vibrational bands at 500 and 590 cm^{-1} at 180 K and 570 and 700 cm^{-1} bands at 230 K, respectively. Based on the isotopic experiment, we assigned these bands to librations of water. Even though, water partially dissociates at 230 K, we were unable to detect a hydroxyl group band both from heating from 180 K to 230 K and in the separate experiment in which hydroxyl group were prepared by dosing water on the surface with preadsorbed oxygen. No Ni-O vibrational mode was detected even at frequencies as low as 200 cm^{-1} . This might be due to the orientation of the bond to the surface. Lower frequencies and broader bands at 180 K are produced by higher coverages, where the non-dissociated water molecules are stabilized by strong dipole-dipole interactions. At 230 K, water does make any clusters or islands. Single molecule is stabilized by hydroxyl groups resulting in higher narrow frequency bands. The O-H group bonds are perpendicular to the surface in both cases.

1. B. W. Callen, K. Griffiths, R. Kasza, M. B. Jensen, P. A. Thiel, P. R. Norton: J. Chem Phys. 97 (1992) 3760.

Figure 1.

FAR-INFRARED SYNCHROTRON SPECTROSCOPY OF FUNCTIONALLY IMPORTANT LOW FREQUENCY MODES IN PROTEINS *

U4IR

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Low frequency modes of proteins arise from (1) large effective masses, resulting from coupled motions of a large number of atoms, and (2) weak bonds, such as hydrogen bonds and salt bridges, which are important for the high-order structure of a protein. We study the structural origins, dynamic nature, and functional roles of low frequency modes of photoactive yellow protein, bacteriorhodopsin, and myoglobin, using far-infrared synchrotron spectroscopy (20 - 500 cm^{-1}), and model compound analysis with homologous amino acid polymers. All proteins examined exhibit broad band absorption with small ripples of narrow bands; while homologous polymers display a few well-defined bands above 60. One band around 110-150 is found in poly-L-Ala, -Leu, and -Trp with dominant α -helical structures, and absent in poly-L-Gly, -Val, and -Phe lacking α -helical structures. Far-infrared difference spectroscopy is being applied to detect changes in collective modes of a protein from one state to another. Discussions will be presented concerning structural origins and biological importance of observed low frequency collective modes in proteins.

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D.-J. Huang and P. D. Johnson, Dept. of Physics BNL

Quantum-size effects on electronic structure have been well studied in semiconductors and transition metals. Recently the quantum well states in the spacer layer of magnetic multilayers have been used to explain the oscillatory exchange coupling. In these magnetic multilayers the exchange coupling between adjacent ferromagnetic layers oscillates with the thickness of spacer layers. The quantum well states in Cu on fcc Co(001) have been found to be spin-polarized, preferentially with minority spin, and crossing the Fermi level with the periodicity identical to the oscillation periods of the exchange coupling in the associated magnetic multilayers. In the present work, we perform photoemission studies of the quantum well states in Cu films deposited on Co and CoNi alloy substrates. The quantum well states in Cu on $\text{Co}_{80}\text{Ni}_{20}$ alloy have been identified, shows that. As shown in Figure 1, these states are less intense and have slightly lower binding energies than those in Cu on Co(001), particularly in the vicinity of the Fermi level. This observation can be well reconciled with the electronic structure change in the substrates. The s-d hybridization gap in $\text{Co}_{80}\text{Ni}_{20}$ alloys moves away from the Fermi level as the Ni concentration increases. Once the Cu quantum well states are located outside of this gap, the reflectivity reduces dramatically and the quantum well states are much less confined. Our results indicate that the degree of quantum confinement can be tuned by altering the electronic structure of magnetic substrates, for instance, changing the relative concentration in the substrate. This in turn suggests the possibility of tuning the exchange coupling strength in the associated magnetic multilayers.

Figure 1. Photoemission spectra of quantum well states in Cu films deposited on $\text{Co}_{80}\text{Ni}_{20}$ and Co substrates. The spectra are taken at normal emission with 23 eV photon energy.

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There is considerable interest in the nature of the bonding between alkali adatoms and metal surfaces. However the magnetic interaction between alkali atoms and ferromagnetic substrates has received less attention. In this work, we use spin-polarized and spin-integrated photoemission spectroscopies to investigate the electronic interactions between chemisorbed Cs atoms and ferromagnetic Fe films which are epitaxially grown on W(110). Spin-integrated Cs 5p photoemission spectra are consistent with previously observed general trends in the coverage dependent binding energy shifts of alkali adatom core-level spectra. The Cs 5p binding energy in the first atomic layer decreases as the Cs coverage increases due to dipolar repulsion and band formation, as shown in Fig. 1. The binding energies of Cs in the second layer are smaller than those in the first layer, an indication that the Cs-Cs interaction is weaker than the Cs-Fe interaction. In addition, the lifetime width of Cs in the first layer is much larger than those in the second layer. This dramatic change of lifetime width is suggestive of s-p hybridization in the first-layer-Cs valence electrons. That no measurable spin-polarization exists in the Cs 5p spectra suggests that there is little or no induced magnetic moment on Cs site, in contrast to the observation of an induced magnetic moment in chemisorbed oxygen and sulfur on ferromagnetic substrates. Data analysis is under way to understand the Cs-Fe electronic interactions.

Figure 1. 5p photoemission spectra of chemisorbed Cs on 10-ML Fe films deposited on W(110). The spectra were taken with 30 eV photon energy and at temperature of 100 K

CORE LEVEL LINESHAPES IN FeRh ALLOY

U7B

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We have carried out photoemission measurements to study the line-shapes of the Fe and Rh core levels – concentrating particularly on 3s and 4s line-shapes, respectively – to monitor the local magnetic character in the antiferromagnetic (AF) and ferromagnetic (FM) states. We have investigated samples of pure Fe, pure Rh and equiatomic FeRh alloy. Characterizations of FeRh samples were done prior to photoemission measurements. X-ray diffraction shows that the FeRh alloy has a CsCl structure and its transition temperature was determined from the electrical resistivity measurements which is in good agreement with previous report.

Figure 1 shows the Fe 3s core levels for pure Fe and FeRh alloy. No change in the line-shapes of the Fe 3s core level in FeRh alloy below and above the transition temperature (350 K). This indicates that the local moment on the Fe sites are same in both AF and FM states which is in agreement with our theoretical calculations using both FSM-ASW (Fixed-Spin Moment, Augmented Spherical Wave) and LMTO (Linear Muffin-Tin Orbital) methods. The Rh 4s core level spectra for both pure Rh and FeRh alloy are shown in figure 2. This preliminary result shows no change in Rh 4s lineshape of FeRh alloy below and above the transition temperature.

One possible reason is that the magnetic properties change significantly from the surface to the bulk for FeRh alloy and theoretical results reflect the bulk magnetic properties while the photoemission measurements reflect the surface properties.

Slab calculations are under way to investigate the possible difference in magnetic properties between bulk and surface for FeRh.

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Figure 1.

Figure 2.

Room-temperature Chlorination of As-rich GaAs(110)

U8A

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It is important to gain an understanding of the reaction of Cl_2 with GaAs since chlorine is the primary chemical etchant used in GaAs device fabrication. The study of Cl_2/GaAs reactions is complicated somewhat by the fact that many GaAs surface stoichiometries are stable and that the composition and crystallinity of the starting surface affect the path of the reaction [1]. For example, in the room-temperature reaction of Cl_2 with GaAs(110), there is a competition between passivation and etching.

GaAs(110) wafers cleaned by chlorination and annealing are found to be slightly As-rich. The subsequent reaction of these As-rich surfaces with Cl_2 is followed over several orders of magnitude in exposure. After low exposures ($< 5 \times 10^4$ L), the surface appears to passivate with only half a monolayer of AsCl formed. Following sufficiently large ($> 5 \times 10^4$ L) exposures, however, the formation of both As and Ga chlorides is observed. After the largest exposures, the distribution of As chlorides still favors the monochloride, but the Ga chlorides favor GaCl_2 , in nearly equal amounts. To explain this result, it is suggested that the surface is terminated by $-\text{AsCl}-\text{GaCl}_2$ moieties. The addition of Cl to form GaCl_3 from GaCl_2 is thus identified as the rate-limiting step in the overall reaction.

Figure 1 shows Ga and As 3d core level spectra collected from As-rich GaAs(110) that was exposed to 1.2×10^6 L of Cl_2 . Indicated in the figure are the individual core-level components that arise from bulk GaAs, GaCl , GaCl_2 , AsCl, and AsCl_2 . Tricoordinate Ga and As atoms also contribute to the spectra, along with Ga clusters, which are thought to generate the low-BE Ga 3d component.

1. W. C. Simpson, D. K. Shuh, W. H. Hung, M. C. H, J. Kanski, U. O. Karlsson, and J. A. Yarmoff, J. Vac. Sci. Technol. A, in press.
2. D. J. D. Sullivan, H. C. Flaum, and A. C. Kummel, J. Chem. Phys. 101 (1994) 1582.

Figure 1.

W.C. Simpson (UC Riverside, MSD LBNL), W.H. Hung (IBM), and J.A. Yarmoff (UC Riverside, MSD LBNL)

The initial stages of the room-temperature reaction of Cl₂ with GaAs(001)-4×6 to form GaCl₃ and AsCl₃ are studied using soft x-ray photoelectron spectroscopy. The results of this investigation are illustrated in Fig. 1, which shows the proportion of the Ga 3d core-level intensity derived from GaCl and GaCl₂ moieties, as well as the proportion of the As 3d core-level intensity arising from AsCl and AsCl₂. Note that exposures were carried out with a solid-state AgCl electrochemical cell, so the Cl₂ dosage is reported in terms of the time-integrated current through the cell, in units of $\mu\text{A}\cdot\text{min}$.

It is found that the coverages of GaCl and AsCl increase linearly with the logarithm of the Cl₂ exposure. This logarithmic exposure dependence of the coverage corresponds to a sticking coefficient that decays exponentially with coverage, as described by the Elovich equation [1], $S(\Theta) = a \exp(-b\Theta)$. The Elovich equation has been used to describe the oxidation of a number of metals, alloys and semiconductors, but it is not supported by a unique microscopic model [2]. Coverage-dependent or reconstruction-dependent activation energies, or the weakening of back-bonds due to chlorine adsorption can all account for this behavior. At this time, further investigation is needed to determine which microscopic model best supports the adsorption kinetics observed for this system.

The appearance of GaCl₂ and AsCl₂ following sufficiently large exposures indicates that chlorination occurs in a step-wise manner. An examination of the Cl 2p level shows that the difference between Cl bound to Ga cannot be resolved from Cl bound to As, but that there is ~ 0.5 eV difference in the Cl 2p binding energy between the monochloride and dichloride moieties.

1. S. R. Morrison, *The Chemical Physics of Surfaces* (Plenum Press, New York, 1990), Ch. 7.

2. G. F. Cerofolini, G. La Bruna and L. Meda, *Appl. Surf. Sci.* 89 (1995) 361.

Figure 1.

W.C. Simpson, J.A. Yarmoff (UC Riverside, MSD LBNL), W.H. Hung, and F.R. McFeely (IBM)

Recent experimental evidence indicates that remote inductive effects may be significant for highly electronegative adsorbates, which would require extending the standard scheme for assigning chemical shifts in Si 2p spectra [1]. To investigate this possibility for halogen systems, Si 2p spectra are collected from monofluorinated and polyfluorinated Si(111) and compared.

Figure 1(a)-(b) shows spectra collected from monofluorinated Si(111) and from the same surface following additional fluorination, which generated higher fluorides. Panel (c) shows the difference between the two, which clearly contains no sub-1-eV shifts. This result restricts the possible types of remotely induced shifts that need to be considered for this system.

For example, the data do not rule out the possibility that 1-eV shifts are induced by -SiF₃ groups, in direct analogy to the 1-eV shifts induced by -SiO₃, seen in ref. [1]. This would alter the interpretation of peak A, in Fig. 1(b). To consider this possibility, an extended set of assignment rules is suggested that is consistent with the data, but which includes the remote inductive effects of F atoms in -SiF₃ groups. It is found that extending the assignment rules in this way does not change the qualitative findings of earlier investigations, but does alter the quantitative results.

1. M. M. Banaszak-Holl, S. Lee, and F. R. McFeely, *Appl. Phys. Lett.* 65 (1994) 1097.

Figure 1.

Electronic Absorption and Luminescence of Adenine Derivatives in Frozen Alcohol Glasses at 77K *

L. A. Kelly and J. C. Sutherland (BNL)

The low temperature electronic absorption and luminescence spectra of purine derivatives have been measured in dilute, hydrogen bonding solvents, at 77 K. The spectra were measured in frozen alcohol glasses of ethanol and 2,2,2-trifluoroethanol at 77 K and the results compared with those obtained for the chromophores in dilute, noble gas matrices (see U11 abstract). The ground-state absorption spectra in the protic glasses were red-shifted by ca. 10 nm with respect to those measured in the noble gas matrices. Upon electronic excitation (200 - 300 nm) of the purine derivatives in the frozen alcohol glasses, both fluorescence (290 - 340 nm) and phosphorescence (350 - 450 nm) were observed from the lowest electronically excited singlet and triplet states, respectively (see Figure 1). In the noble gas matrices, only the long-lived phosphorescence was observed. The results indicate a dramatic solvent effect on the photophysical properties of the electronically excited states and, in particular, enhanced fluorescence quantum yields in the protic solvents. We have measured the fluorescence lifetimes of the adenine, 7-methyladenine, and 9-methyladenine to be 2.22 ns, 2.19 ns, and 1.35 ns, respectively, in frozen ethanol at 77K.

Figure 1. Time-resolved luminescence spectrum of adenine in frozen ethanol glass at 77K following excitation with 260 nm pulsed synchrotron light (5 bunches shown). The 3-D representation clearly shows the UV fluorescence at short wavelengths and long-lived phosphorescence at longer wavelengths of the emission spectrum.

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Secondary Structure of the Pleckstrin Homology Domain of PLC- δ

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This study involved determining the secondary structure of the pleckstrin homology (PH) domain of phospholipase C - δ (PLC- δ). PH domains have been identified in over seventy proteins. Although these domains have little sequence homology, their tertiary structure appears to be well conserved (for background see Ferguson et al. (1995) *Struc.Biol.* 2, 715-718). PH domains are thought to function as modular units that either enhance the binding of the intact protein to the beta-gamma units of guanine nucleotide exchange proteins (G proteins) or to membranes containing phosphatidylinositol 4,5-bisphosphate (PIP₂). Structural studies the PH domains of two proteins have been solved and have been shown to consist of two pairs of beta-sheets and an alpha helix. To gain knowledge about the secondary structure of the PH domain of PLC, we determined the CD spectra in the presence and absence of PIP₂. We find that this protein has a much higher helical content than the PH domains of the other two proteins, and that the structure changes little in the presence of PIP₂-containing membranes. This work has been accepted for publication (Garcia et al., *Biochemistry*)

Effect of Increased Lipid Packing on the Conformational State of GLUT1	U9B
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In this study we used the optical facilities at BNL to measure the fluorescence lifetimes of the tryptophan residues of the facilitative glucose transporter (GLUT1). Glucose binding to GLUT1 results in a structural change to an active conformation. The goal of this project was to determine whether increased lipid packing would stabilize this state. We and others have found that the fluorescence emission intensity and anisotropy are highly sensitive to GLUT1 conformation. To determine whether these changes are a result of changes in fluorescence lifetime, we measured this parameter under various conditions. These measurements served to be valuable in determining that the binding of glucose statically quenches GLUT1 fluorescence due to a movement of the interfacial tryptophan residues towards the ionic groups on the membrane surface and that increased lipid packing stabilizes this state. This work has been recently published Scarlata et al. (1995) Biochemistry 34, 7703-7711.

Solution Circular Dichroism of 1,6-Anhydroglucopyranoside	U11
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E.R. Arndt and E.S. Stevens (SUNY Binghamton)

The Circular Dichroism (CD) spectrum of 1,6 anhydroglucopyranoside as prototypical of anhydrosugars was measured over the range of 170 to 230nm. A negative CD band was found at 183nm with a shoulder at 195 nm. A cross-over occurs at 176nm, and the CD remains positive to the solvent limit. The spectrum strongly resembles that of a methyl- β -D-glucopyranoside film, except that the features are red-shifted approximately 7 nm in the anhydrosugar. The presence of the five membered ring is obviously implicated in the shift. [Supported by NIH Grant GM46455]

Figure 1. 7.55 mg/ml Anhydroglucoside (aglu) in a 50 micron cell.

Photoionization Study of Ethanol and Radicals Derived From Ethanol: Theory and Experiment

U11

D. J. Bogan, F. L. Nesbitt, L. J. Stief (NASA/Goddard), J. L. Durant (SNL), S. C. Kuo, Z. Zhang and R. B. Klemm (BNL)

This study includes theoretical and experimental results for the ionization energies (IE) of ethanol, ethoxy radical, 1-hydroxyethyl radical, and the appearance energy (AE) of 1-hydroxyethyl cation from ethanol. Experimental measurements were obtained at the NSLS using a discharge flow-photoionization mass spectrometer (DF-PIMS) apparatus. Ab initio calculations were done at Sandia National Laboratory using the Gaussian-2 (G-2) method, which is a well characterized theoretical procedure which has been shown to yield accurate bond strengths and ionization energies. G-2 is a composite procedure that approximates a QCISD(T)/6-311+G(3df,2p) calculation as a linear combination of smaller calculations.

All experiments were conducted at 300K with a flow tube pressure of about 4 Torr of helium and at flow velocities of about 1000 cm/s. Hydroxyethyl radicals, C_2H_4OH or C_2D_4OH , were generated by the reaction of F atoms with ethanol, C_2H_5OH or C_2D_5OH . Ethoxy radicals, C_2D_5O , were produced by the reaction of C_2D_5 with NO_2 via the reaction sequence: $F + C_2D_5 \rightarrow C_2D_5 + DF$; $C_2D_5 + NO_2 \rightarrow C_2D_5O + NO$. Radical concentrations in the flow reactor were 10^{12} to 10^{13} molec./cm³. Photoionization efficiency (PIE) spectra were obtained by plotting the ratio ions/light as a function of wavelength. Analysis of the PIE curves yielded the following results that are compared to the calculated values in Table 1. The experimental uncertainty is ± 0.05 eV or less in all cases. It was assumed that the lowest energy AE for loss of one hydrogen from ethanol gives 1-hydroxyethyl cation, and that $IE(CH_3CHOH) < IE(CH_2CH_2OH)$. IE's for 1-hydroxyethyl radicals and ethoxy radical were obtained from thresholds that displayed weak step-like behavior. AE's for CH_3CHOH^+ and CD_3CDOH^+ from dissociative ionization of the corresponding alcohol were measured from linearly ascending thresholds.

The work at BNL was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC02-76CH00016.

Neutral	Ion	Experiment	Theory
C_2H_5OH	$C_2H_5OH^+$	10.43	10.41
C_2D_5OH	$C_2D_5OH^+$	10.46	10.40
CH_3CHOH	CH_3CHOH^+	6.73	6.68
CD_3CDOH	CD_3CDOH^+	6.70	6.67
C_2H_5OH	CH_3CHOH^+	10.81	10.79
C_2D_5OH	CD_3CDOH^+	10.93	10.89
C_2D_5O	$C_2D_5O^+$	10.37	10.32

Figure 1. Ionization Energy or Appearance Energy (in eV).

Electronic Spectroscopy of Matrix-Isolated Adenine Derivatives at 12 K *

U11

L. A. Kelly, E. D. Johnson, J. C. Sutherland (BNL)

Low temperature fluorescence and UV/VUV absorption measurements of purine and indole derivatives, isolated in argon matrices at 12K, have been carried out at beamline U11. Purine and indole derived chromophores are important light absorbing species in nucleic acids and proteins, respectively, of biological systems. Hence, the investigations were carried out to assess the fate of the initially produced electronically excited states subsequent to UV and VUV photon absorption. The matrix isolation experiments provide a means of investigating the spectroscopic properties of the isolated chromophores in a non-hydrogen bonding solvent.

The substrates were isolated in condensed argon matrices at 12K, which served as transparent hosts down to 105 nm. Both steady-state and time-resolved luminescence measurements were carried out. No fluorescence was observed from the electronically excited singlet state of the purine and adenine derivatives. The observed emission was independent of excitation wavelength and was characterized as structured, long-lived phosphorescence from the lowest electronically excited triplet state of adenine (Figure 1). Since adenine is known to exist as a mixture of N(7)-H and N(9)-H tautomers, we investigated the N-7 and N-9 methylated adenine derivatives as tautomer models. The absorption (Figure 1), excitation, and emission spectra (not shown) of 9-methyladenine were found to be quite similar to that of adenine. However, the emission spectrum of 7-methyladenine was significantly blue-shifted with respect to both adenine and 9-methyladenine, suggesting that the N(9)-H tautomer is the major tautomer in matrix-isolated adenine.

Figure 1. (a) Ground-state absorption spectra of argon matrix-isolated adenine (solid line) and 9-methyladenine (dashed line) at 12 K; (b) Emission spectra of adenine (solid line) and 7-methyladenine (dotted line) in argon matrices at 12 K.

* This work was supported by the U.S. DOE, Office of Health and Environmental Research, and the National Synchrotron Light Source. L.A.K. acknowledges the DOE Distinguished Postdoctoral Fellowship Program, administered by the Oak Ridge Institute for Science and Education, for support.

A Discharge Flow-Photoionization Mass Spectrometric Study of HOI: Photoionization Efficiency Spectrum and Ionization Energy

U11

P. S. Monks, L. J. Stief (NASA/Goddard), D. C. Tardy (Univ. Iowa), J. F. Liebman (Univ. Maryland/Balto. Co.), Z. Zhang, S. C. Kuo and R. B. Klemm (BNL)

Photoionization efficiency (PIE) spectra of HOI were measured over the wavelength range $\lambda = 115$ to 130 nm (Fig. 1) and in the ionization threshold region, $\lambda = 123$ to 129 nm (Fig. 2), using a discharge flow-photoionization mass spectrometer apparatus coupled to a synchrotron radiation source. HOI was generated, in situ but in varying amounts, by three separate reactions: $\text{OH} + \text{I}_2$; $\text{OH} + \text{CF}_3\text{I}$; and $\text{O}(^3\text{P}) + \text{C}_2\text{H}_5\text{I}$. The PIE spectra displayed step-like behavior near threshold and the HO-I stretching frequency in the cation was determined to be $702 \pm 60 \text{ cm}^{-1}$. A value of $(9.81 \pm 0.02) \text{ eV}$ was obtained for the adiabatic ionization energy (IE) of HOI from photoion thresholds, corresponding to the $\text{HOI}^+(\text{X}^2\text{A}''') \leftarrow \text{HOI}(\text{X}^1\text{A}')$ transition. Even though the present result appears to be the first reported determination of IE(HOI), the experimental value is compared with an estimated value previously derived via a trend analysis and it is considered in terms of trends in the series IE(HOX), where X = F, Cl, Br and I. The branching ratio for $[\text{HOI}]/[\text{IO}]$ in the $\text{O}(^3\text{P}) + \text{C}_2\text{H}_5\text{I}$ reaction was estimated to be about 8/1 at $T = 298 \text{ K}$, if we assume that the photoionization efficiencies for HOI and IO are the same at 10.3 eV ($\lambda = 120 \text{ nm}$).

The work at BNL was supported by the Chemical Sciences Division, Office of Basic Energy Sciences, U.S. DOE, under contract No. DE-AC02-76CH00016.

Figure 1. Photoionization efficiency spectra of HOI between $\lambda = 115.0$ and 130.0 nm at 0.2 nm steps. The HOI molecule was produced in (a): by the reaction $\text{O}(^3\text{P}) + \text{C}_2\text{H}_5\text{I}$; and in (b): by the reaction $\text{OH} + \text{CF}_3\text{I}$. The positions of the "steps" in the PIE curves (126.3 nm , 125.2 nm and 124.1 nm) are indicated by the superposed lines.

Figure 2. Photoionization threshold region of HOI at a nominal resolution of 0.13 nm and 0.1 nm steps between $\lambda = 123.0$ and 129.0 nm . The onset of ionization is at $\lambda = 126.35 \text{ nm}$ ($9.813 \pm 0.010 \text{ eV}$).

Experimental Determination of the Ionization Energy of $\text{IO}(\text{X}^2\Pi_{3/2})$ and Estimations of $\Delta_f H^\circ(\text{IO}^+)$ and $\text{PA}(\text{IO})$

U11

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Photoionization efficiency (PIE) spectra of $\text{IO}(\text{X}^2\Pi_i)$ were measured over the wavelength range $\lambda = 115.0$ to 130.0 nm (Fig. 1) and in the ionization threshold region, $\lambda = 126.0$ to 130.0 nm (Fig. 2), using a discharge flow-photoionization mass spectrometer apparatus coupled to a synchrotron radiation source. Iodine oxide was generated by the reactions of $\text{O}(^3\text{P})$ atoms with I_2 and CF_3I . The PIE spectra displayed step-function behavior. From the half-rise point of the initial step, a value of $9.73 \pm 0.017 \text{ eV}$ was obtained for the adiabatic ionization energy (IE) of IO, corresponding to the $\text{IO}^+(\text{X}^3\Sigma^-) \leftarrow \text{IO}(\text{X}^2\Pi_{3/2})$ transition. The separation between the first two steps in the PIE spectrum (which might be perturbed slightly due to autoionization) was used to derive the vibrational spacing of the cation, $1060 \pm 160 \text{ cm}^{-1}$. A Rydberg progression, presumably converging to the excited $^1\Delta$ state of the cation, has a convergence limit that lies 0.596 eV above the ground state of the cation. A selected value for the bond dissociation energy of IO, $D^\circ_0(\text{IO}) = 226 \text{ kJ mol}^{-1}$, leads to $\Delta_f H^\circ(\text{IO}) = 128 \pm 4 \text{ kJ mol}^{-1}$. From this value for the heat of formation of IO, estimates are made for $\Delta_f H^\circ(\text{IO}^+)$, $\Delta_f H^\circ(\text{HOI})$ and the proton affinity of IO.

The work at BNL was supported by the Chemical Sciences Division, Office of Basic Energy Sciences, U.S. DOE, under contract No. DE-AC02-76CH00016.

Figure 1. Photoionization efficiency spectrum of $\text{IO} (m/z = 143)$ between $\lambda = 115.0$ and 130.0 nm . The arrow indicates the onset of ionization at 127.3 nm ($\text{IE} = 9.74 \pm 0.02 \text{ eV}$). The superposed lines indicate autoionization which presumably correlates with a Rydberg progression that converges to an excited state of the cation at 120.0 nm (10.332 eV).

Figure 2. (A) Photoionization threshold region of $\text{IO} (m/z = 143)$ at a nominal resolution of 0.23 nm and 0.1 nm steps between $\lambda = 126.0$ and 130.0 nm . (B) Energy derivative of (A). The maximum in the derivative is at $\lambda = 127.35 \text{ nm}$ ($9.73 \pm 0.018 \text{ eV}$).

The electronic structure of Be(10-10)

U12

Ph. Hofmann and E.W. Plummer (ORNL and University of Tennessee)

Beryllium is a simple metal with most unusual properties both in the bulk and at the surfaces. In the bulk the electronic density of states has a minimum at the Fermi-level indicating large deviations from free-electron like bonding. As a consequence many structural and elastic properties are anomalous. At the closed packed (0001) surface the free-electron like density of states is large due to a surface state and the first layer behaves more like a free electron metal [1]. Cleaved perpendicular to the (10-10) direction the bulk crystal can show two different terminations whose first interlayer spacing differs by a factor of two. In what follows these terminations are called the "long" and the "short" termination. A recent calculation by Chulkov [2] predicts an even higher free-electron like density of states at this surface independent from the type of termination. However, the predicted surface band dispersion is clearly different for both terminations. Measuring the surface electronic structure will hence give the type of termination and some indications as to the reliability of the local density approximation to determine surface state dispersions.

We have determined the electronic structure of Be(10-10) with angle resolved photoemission. Our results clearly rule out the long termination and the experimentally determined dispersion of the surface states is given in Fig. 1 superimposed on the Chulkov's calculation for the short termination. The major difference between calculation and experiment is that the two predicted surface states at the L point are not observed. This is probably due to a slight error in the energy of the projected bulk bands due to many body interactions.

[1] E.W. Plummer and J.B. Hannon, Prog. Surf. Sci. 46, 149 (1994).

[2] E.V. Chulkov, to be published.

Figure 1. Surface state dispersion on Be(10-10). The experimental points (markers) are superimposed on the calculation for the short termination from Ref. [2].

Quantitative Calcium XANES *

U13UA

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The absorption spectra of five biologically significant calcium salts were recorded in total electron yield (TEY) mode at the Ca L edge. These spectra, taken at beamline U13UA, are to be used to assess the feasibility of generating spatial maps with chemical state contrast from calcified tissue imaged in transmission on the scanning transmission x-ray microscope (STXM) at beamline X1A[1]. Drift in energy locations were corrected using CaF_2 standards. Quantification was attempted in a two-stage process. Firstly the pre- and post-continuum step 'plateau' regions were fitted to cross-sections for the salt (using nominal composition and tabulated elemental values) plus an area fraction of substrate. The fitting was repeated with the additional constraint of constancy of a calcium equivalent peak integral. At both stages, spectra showing signs of distortion were rejected.

Fig. 1 shows the calcium equivalent spectra for one series of experimental conditions. The details show the NEXAFS minor peak structure which precedes the main peaks. It is this structure which shows the variation between salts which we hope to exploit for chemical state mapping in the STXM.

[1] C. J. Buckley, S. J. Bellamy, X. Zhang, G. Dermody and S. L. Hulbert, Rev. Sci. Instrum. 66, 1322 (1995).

Figure 1. Calcium salt absorption spectra (from total electron yield signal).

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Thermal and Photochemical Deposition of Sulfur on GaAs(100) * U13UA

S. Conrad, Q.-S. Xin, X.-Y. Zhu (Southern Ill. Univ.) and D. R. Mullins (ORNL)

The interaction of sulfur with GaAs(100) is of great interest due to its importance in surface passivation. We have investigated the thermal and photochemical deposition of S on GaAs(100) from H₂S using soft x-ray photoelectron spectroscopy (SXPS). The deposition of S can be achieved by exposing GaAs(100) to H₂S at substrate temperatures ≥ 550 K, a result of the irreversible dissociation of H₂S on the surface. Both the rate and extent of sulfur deposition is enhanced by white light synchrotron radiation. More than twice as much S was deposited using eight cycles of dose/irradiate/anneal compared to the saturation S coverage obtainable by thermal decomposition alone. The photoassisted deposition showed no evidence of saturation.

Heating of S covered GaAs(100) to ≥ 700 K results in a well ordered (2x1) surface reconstruction, as evidenced by low energy electron diffraction (LEED). This high temperature stabilized surface is characterized by two well defined states of S, both bonded to Ga atoms. One state can be attributed to surface gallium sulfide while the other to sub-surface S which replaces As atoms. This interpretation is supported by the observation that the As/Ga ratio, as determined by the 3p SXPS peak intensities, decreases linearly with increasing S coverage.

Resolution test of U13UA 160°-included angle grating

U13UA

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In addition to the 174°-included angle gratings (300, 600, and 1200 lines/mm) typical of now-"standard" Spherical Grating Monochromators (SGM), two 160°-included angle gratings (600 and 1200 lines/mm) have been installed and commissioned at beamline U13UA. These latter two "low-energy" gratings require two post-deflecting mirrors, at 12° downward-deflecting and 5° upward-deflecting grazing angles of incidence, to make the diffracted beam coincident with that of the 174°-included angle "high-energy" gratings.

The photon energy range covered by the low-energy gratings is 20-150 eV. One of the best photon-energy resolution tests in this photon energy range is to measure the double-excitation Rydberg resonances of He below the N=2 threshold of He⁺, as shown for the SX700 monochromator at BESSY by Domke, et al. [Phys. Rev. Lett. 69, 1171 (1992)] and, more recently, for a standard SGM at ALS by Kaindl, et al. [abstract for VUV XI, Tokyo, 1995].

As a resolution test, this series was measured using the 600 line/mm low-energy grating at U13UA and a purpose-built gas cell filled with 25mTorr He. As shown in Fig. 1, the (sp,2n+) states are observable out to n=13, which corresponds to a resolving power of at least 5000. This resolution is quite good, considering that there are three resolution-determining optical elements in this branch of U13UA (an SGM designed specifically for this photon energy range would use only a single resolution-determining optical element).

Figure 1. Autoionizing resonances of doubly excited Helium below the N=2 threshold (IP₂) of He⁺. The (sp,2n+) states are seen out to n=13, which corresponds to a resolving power ≥ 5000 .

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Ratio of Double-to-Single Photoionization of Helium from Threshold to 700 eV *

U13UA

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Theoretical prediction of the energy dependence of the double ionization of helium by a single photon is a fundamental problem in atomic physics which requires solution of the Coulomb three-body problem. In the independent-particle framework, in which the photon can interact directly with only one electron, double ionization by a single photon can proceed only by electron-electron correlation. As a result, photoionization of helium has long been used as a testing ground for understanding correlation phenomena.

Despite the importance of the problem, and the abundance of widely varying theoretical predictions at all energies, available data are definitive only for a few eV above the double-ionization threshold (79 eV), where the ratio of double-to-single ionization of helium has been shown to be in good agreement with Wannier Theory. Nevertheless, available theories and measurements essentially span the space between the two theoretical curves shown in Fig. 2. It was the goal of our work on U13UA to obtain an accurate determination of the energy-dependent ratio of double-to-single photoionization of helium from threshold to 700 eV.

Figure 1 illustrates a spectrum obtained at 200 eV. Shown are both charge states of helium along with a prompt signal due to Rayleigh (elastic) scattering of photons from the target gas. Care was taken to assure that low energy light from the monochromator or collimating slit assemblies was filtered from the beam.

Our measured ratios have smaller statistical errors than previous results, and show a broad maximum at about 180 eV. Ratios reported here are typically 10% lower than earlier measurements.

Figure 1. Time-of-flight spectrum of helium obtained with 200 eV photons.

* Work supported by NSF

Adsorption and Reaction of Methanethiol on Ni Covered W(001)

U13UA

D. R. Mullins (Oak Ridge National Lab)

The adsorption and reaction of methanethiol, CH_3SH , has been studied on Ni covered W(001). The Ni films varied in thickness from sub-monolayer to multilayer. CH_3SH follows two competing reaction pathways on these surfaces. It can undergo non-selective total decomposition producing adsorbed S and C and desorbed H_2 , or it can produce CH_4 through selective decomposition. As the Ni coverage is increased, the percentage of selective decomposition, as indicated by the relative amount of methane desorbed, increases. On the clean surface less than 40% of the adsorbed thiol produces methane. This percentage rises to ca. 70% on a surface with 1 ML of Ni, and to ca. 85% when 2 ML of Ni are preadsorbed. The CH_4 desorption temperature also drops from 370 K to 290 K to 210 K on 0, 1 and 2 ML Ni surfaces, respectively.

S 2p and C 1s core level photoemission was used to identify reaction intermediates on the surface during decomposition and to determine the temperature at which C-S bond scission occurs. At all Ni coverages, two methyl thiolate species (CH_3S) are observed in the S 2p spectra. These are assigned to thiolates in hollow and bridge sites. The S 2p peak positions are about the same on 1 and 2 ML of Ni. The relative amount of CH_3S adsorbed in the lower binding energy, bridge site is greater on 2 ML of Ni, however. The C 1s spectra indicate that no C-S bond scission occurs at 100 K on 0 and 1 ML of Ni. Ca. 10% of the CH_3S decomposes at 100 K on 2 ML of Ni producing a surface methyl group that later desorbs as methane.

These results are consistent with what has been observed on many other clean metal surfaces. Specifically, multiple thiolate adsorption sites are common, C-S bond scission occurs at about the same temperature as methane desorption and, in general, a lower bond activation temperature promotes selective decomposition. A surprising result is that the CH_3S S 2p peaks on the Ni films had a lower binding energy than CH_3S on either W(001) or Ni(001). The S 2p peaks for atomic S on the Ni films had a binding energy that was between the values observed on W(001) and Ni(001). The low binding energy for the thiolates may be correlated with the lower C-S bond scission temperature observed on the Ni films.

Figure 2. Comparison of present results with two early theoretical predictions

* Research supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

D. R. Mullins (Oak Ridge National Lab)

Methanethiol (CH₃SH) adsorbs as methylthiolate (CH₃S) on Ni(111) at 100 K. When the sample is heated to 250 K, some of the thiolate decomposes forming atomic S and some is transformed into a thiolate with a much lower S 2p binding energy. The difference between these two thiolates is not known for certain. Based on the relative binding energies, it was hypothesized that the CH₃S formed at 100 K adsorbed in a lower coordination binding site than the thiolate formed at 200 K. Angle resolved photoelectron diffraction experiments have been performed utilizing the S 2p photoemission from these two states in order to determine their adsorption sites and the orientation of the C-S bond.

Atomic S is known to adsorb in the FCC 3-fold hollow site on Ni(111). The sample was mounted so that the Ni-S bond axis aligned along the emission direction as the sample was rotated. The first panel shows the relative S 2p intensity at different emission angles for an electron emitted with a kinetic energy of 200 eV. The enhanced emission near 40 deg. is the result of backscattering from the Ni surface atom. The absence of enhanced emission at 0 deg. indicates that S is adsorbed in the FCC hollow with no second layer Ni atom beneath it. The S 2p angular dependence from CH₃S formed at 100 K is shown in the second panel. The pattern is qualitatively similar to the angular dependence from atomic S, indicating that the CH₃S is adsorbed in the FCC hollow site and that the C-S bond is not oriented normal to the surface. The S 2p angular dependence for CH₃S formed at 250 K is shown in the third panel. This result suggests that this thiolate is not adsorbed in the FCC site. Results at higher photoelectron kinetic energies indicate that the enhanced emission at 0 deg. is due to forward scattering along the C-S bond which is oriented normal to the surface.

Figure 1.

* Research supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

D. R. Mullins and S. H. Overbury (Oak Ridge National Lab)

The coadsorption of S and Ni on W(001) was studied using S 2p photoemission. Figure 1 shows an annealing set for 0.5 ML of Ni deposited at 100 K on 0.5 ML of S on W(001). The bottom spectrum is from S on clean W(001). At 100 K two new S 2p states appear with S 2p_{3/2} binding energies of 161.55 and 162.00. When the sample is annealed to 500 K, the 161.55 eV state disappears and the 162.00 eV state increases in intensity. We interpret the 161.55 eV state as interface S, residing either underneath or next to the adsorbed Ni. The 162.00 eV state results from S on top of the Ni film. When the sample is annealed to 1000 K, the signals from S on W(001) and S on the Ni film merge into a new, broader state with a S 2p_{3/2} binding energy of 162.45 eV. This new state is attributed to S adsorbed on a Ni / W(001) surface alloy which is known to form near 750 K when the Ni coverage is less than 1 ML.

Figure 2 shows S 2p spectra for various coverages of Ni deposited at 100 K on < 0.5 ML of S on W(001) and then annealed to 1000 K. It can be seen that each coverage results in a distinct S 2p state. When the Ni coverage is 0.5 ML, the S 2p signal has a binding energy that is closest to the S 2p peak position on W(001). An unexpected result is that the S on 2 ML of Ni has a higher binding energy (closer to the position on W(001)) than S on 1 ML of Ni. At intermediate coverages, multiple states are observed reflecting S adsorbed on patches of clean W, Ni/W alloy, 1 ML of Ni and 2 ML of Ni.

Figure 1.

Figure 2.

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We report the first on- L_3 -resonant ($2p_{3/2} \rightarrow 3d^*$) spin-resolved Auger electron spectra (SPAES). By comparing the measured net spin polarization of Fe core-valence-valence (CVV) Auger electrons excited by on- and off- L_3 -resonant photons with the calculated Fe valence band spin polarization, we address the question: to what extent are spin-dependent interactions, or exchange correlations, present in band-like ferromagnetic metals such as Fe. The main difference between on- and off-resonant CVV Auger processes is in the degree of spin polarization of the initial core hole, which for Fe is highly polarized on-resonance and nearly completely unpolarized off-resonance. Correlation between this core hole and the valence electrons can be measured via the spin polarization of the outgoing CVV Auger electron. However, if correlation effects are not significant for Fe, the spin polarization will be equal to the polarization of the valence electrons $P_{VB}=0.27$.

The principal results of our SPAES experiments on Fe, taken using the NYU spin-resolving electron spectrometer, are shown in Figs. 1 and 2. Although the shapes of all four measured spectra in Fig. 1 (symbols) agree with the calculated spectra (lines), the degree of spin polarization on-resonance ($P_{on}=0.37$, Fig. 1(a)) is significantly greater than P_{VB} , whereas the off-resonance value ($P_{off}=0.20$, Fig. 1(b)) is significantly lower than P_{VB} . These findings are consistent with the triplet final-state Auger matrix element being significantly weaker than that of the singlet state (singlet/triplet $\approx 3/2$). This, in turn, can be interpreted as being due to a Fermi hole, or a spin-spin electron correlation responsible for keeping equal spins further apart, effectively lowering the triplet Auger probability.

We suggest that this is a general phenomenon, as depicted in Fig. 2: SPAES carries important information both on the spin polarization of the valence band and the relative strength of exchange correlation. In particular, SPAES demonstrates the importance of exchange correlation in itinerant 3d-metals such as Fe.

Figure 1. (a) Majority-spin (Δ) and minority-spin ($\circ$) off-resonance Fe $L_3M_{45}M_{45}$ Auger electron spectra ($h\nu=820\text{eV}$) from a $30\text{\AA}$ Fe/Ag(001) film, and the convolution of majority-spin (solid line) and minority-spin (dashed line) broadened (1.5eV) Fe density-of-states (DOS) with total Fe-DOS. (b) as in (a) except using on-resonant excitation ($h\nu=707\text{eV}$). The shaded region represents the direct Fe valence band photoemission.

Figure 2. Calculated spin polarization of the Fe CVV Auger transition as a function of Auger matrix element amplitude (strength of electron-electron exchange correlation, or singlet/triplet probability) and of initial core-hole spin polarization. The measured electron-energy-integrated spin polarizations of Fe $L_3M_{45}M_{45}$ Auger spectra on-resonance ($h\nu=707\text{eV}$; $\bullet$) and off-resonance ($h\nu=820\text{eV}$; $\circ$) are shown.

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It is considered a requirement to characterize the imaging optics used in Extreme Ultraviolet Lithography (EUVL) with the light that they image. Therefore there is a requirement to develop interferometry techniques that operate at 13nm wavelength. We have built an 'At Wavelength' interferometer on U13UB to develop such technology. We have carried out the initial measurements that demonstrate that this interferometer is able to characterize the wavefront phase to an accuracy of 0.02waves rms at a wavelength of 13nm . This was achieved by analyzing the spherical wavefront generated by illuminating a pinhole (diameter = 2.5micron). The light that passes through the pinhole undergoes diffraction and yields a characteristic Airy pattern on an area CCD detector placed after the pinhole. This spherical wavefront acts a source that can then be used to test whether the interferometry works. The interferometry technique used is shearing interferometry (1) where the wavefront is diffracted from a grating and the zero and first orders are allowed to interfere. In this way the wavefront acts as a reference to itself.

The experimental setup consists of a grating placed about 4mm beyond the pinhole and the transmitted light is collected by a CCD. Figure 1 shows the interference pattern formed on the CCD. The light is diffracted in the vertical plane and the image shows the overlap of zero, $+1$ and -1 orders. The horizontal bars are the interference patterns. The mode of data collection is the phase shifting interferometric technique (2) whereby the grating is shifted $\pi/4$ of a period and an interferogram recorded for each grating position. We have developed the code that allows us to analyze these interferograms. By analyzing interferograms from orthogonal gratings and stitching the results together a 3D map of the phase of the wavefront can be generated. Figure 2 shows such a plot of the wavefront. It shows the wavefront phase where the spherical wavefront is cut by the grating positioned after the pinhole. The shape is expected to be a parabola (i.e. defocus - the 'focus' for a pinhole optic is at the pinhole) and the analysis code yields a departure from pure defocus behavior by 0.02 waves rms over the full surface. Such a sensitivity is adequate to characterize the wavefront of an EUVL camera.

1. "Optical Shop Testing". Chapter 4. M.V.Mantravadi, Wiley Interscience Pub. (1992), D.Malacara (ed).

2. "Optical Shop Testing". Chapter 14. J.E.Greivenkamp, J.H.Brunning, Wiley Interscience Pub. (1992), D.Malacara (ed)

Figure 1. EUV Shearing Interferograms of a spherical wavefront for 5 different positions of the shearing grating.

Figure 2. 3D map of the measured phase of the spherical wavefront.

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By using monochromatic soft x-rays it is possible to excite or ionize core electrons in molecules selectively. The atomic site of the core hole and the electronic configuration of the core hole final state can be selected by tuning the photon energy to various bound state resonances or into the ionization continuum.

The consequences of such excitation for various molecules (e.g. nitrous oxide, acetone, benzaldehyde, cyanobenzene, cyanobenzaldehyde) in different cryogenic matrix environments are being elucidated. A deuterium matrix at 4.5 K is used to minimize ionization of the host material, and Fourier transform infrared spectroscopy is used to monitor the chemical reactions.

For example, nitrous oxide deposited in a matrix at 4.5 K at a concentration of 0.5% is irradiated with soft x-rays (380 eV) below the nitrogen 1s-ionization threshold, at the nitrogen and oxygen 1s-ionization edges (405 and 535 eV), and in the nitrogen and oxygen 1s-ionization continua (425 and 560 eV). In a deuterium matrix the dominant reaction products formed at all photon energies are D_2O , DO_2^+ , and OD. In a neon matrix various nitrogen oxides (NO , NO_2 , N_2O_3 , $N_2O_2^-$, NO_2 , and NO_2^+) are formed with $N_2O_2^-$, N_2O_3 , and NO_2 being formed only at the ionization edges. No photoproducts appear in the infrared spectra with irradiation at 380 eV, which is below the threshold for core electron excitation. This result indicates that the chemistry results from core electron excitation and not from valence ionization of either the guest or the matrix molecules.

Measurements of quantum yield, the concentration dependence, and the effects of deposition and annealing conditions are being used to determine the reaction mechanisms that produce these products.

Figure 1. Difference Infrared Spectra of N_2O in Deuterium, Neon and Argon matrices irradiated with Soft X-rays and Electron Beam.

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X-ray Absorption Near Edge Structure (XANES) of poly(ethylene terephthalate) (PET) and polyarylate (PAR)

X1A

H. Ade, A. P. Smith, V. Zhuang (NCSU), D.-J. Liu, J. Marty, A. Monisera, and J. Chung (Allied Signal)

We have acquired high resolution XANES spectra of poly(ethylene terephthalate) (PET) and polyarylate (PAR) which will serve the following dual purpose: (i) they will allow us to better understand the spectroscopy of relatively complex polymers by revealing subtleties of the XANES due to the higher energy resolution achieved, (ii) they will serve as model spectra for comparison with spectra to be acquired from PET/PAR blends. In the latter study the objective will be to determine the respective partial dissolution of these polymers in phase separated polymer blends composed of the two polymers as a function of blend composition. The fitted spectra are shown in Figure 1, while the chemical structure is displayed in Figure 2. We are in the process to assign all spectral features needed to provide the best fit. Several of the low intensity features have not been seen previously. Unfortunately, data acquired from other reference samples shows that there is a preferential orientation in these samples and hence some polarization dependence. This will complicate a fully quantitative analysis of the dissolution in blends of these polymers, but will not affect the spectroscopic assignment.

1. Work supported in part by NSF Young Investigator Award, DMR-9458060 (HA). We thank H. Chapman for his help during some of the data acquisition.

Figure 1. XANES spectra of PET and PAR

Figure 2. Chemical structures of PET and PAR

X-ray Absorption Near Edge Structure (XANES) of polyethylene (PE) and polypropylene (PP).

X1A

H. Ade, V. Zhuang, A. P. Smith (NCSU), and P. Schmitz (Ford Motor Co)

Polyolefine polymers and polymer blends are extensively utilized in the automotive industry. We are in particular interested in characterizing the morphology of PP and PP-co-PE polymer blends in the bulk and near surfaces in order to understand its effect on paint adhesion. We have thus acquired XANES spectra of polyethylene (PE) and polypropylene (PP) with the X1-STXM. Since both polymers are aliphatic and contain predominantly saturated bonds the expected differences are very small. Only the relative ratio of C-C and C-H bonds should be slightly different in these materials. The XANES spectra as acquired with the X1-STXM are shown in Figure 1. PE has clearly a double peak near 288 eV, and additional structure above 290 eV, while the respective regions in PP are much more rounded and smooth. (We are not aware of any work in which the double peak feature in PE has been observed previously). These spectra were acquired from an area about 30 microns square and should therefore represent an average of micro-crystalline regions in the PE. Nevertheless, the PE spectrum might exhibit some polarization dependence related to preferential orientation of the material due to sectioning rather than be representative of an isotropic material. The spectral features near 285 eV are only partly due to imperfect I-zero normalization which is confined to this energy range. It also reflects a low concentration of double bonds in these materials, possibly caused by radiation damage. The spectral differences observed make us hopeful to be able to study the polymer blends of interest with the X1-STXM.

1. Work supported in part by NSF Young Investigator Award, DMR-9458060 (HA). We are grateful to R. Spontak for sectioning these materials.

Figure 1. XANES spectra of PE and PP

CARBON IMAGING AND CARBON-XANES MEASUREMENTS ON AN INTERPLANETARY DUST PARTICLE.

X1A

Saša Bajt (U. of Chicago), Henry N. Chapman (SUNY at Stony Brook), George J. Flynn (SUNY at Plattsburgh), and Lindsay P. Keller (MVA Inc.).

The nature and distribution of carbon in interplanetary dust particles (IDPs) are important because IDP carbon has been proposed as a major source of pre-biotic organic material on the early Earth (1) and may have been equally important on the surface of early Mars (2). Both the abundance and the types of carbon in IDPs have exobiology implications.

An $\sim 12 \mu\text{m}$ chondritic-porous IDP (L2008F4) was embedded in sulfur and microtomed into thin sections, $\sim 80 \text{ nm}$ thick. The sections were analysed using the scanning transmission x-ray microscope (STXM) at beam-line X1A. High resolution images of an IDP section were taken at energies above and below the carbon K-edge. By taking differences in the logarithm of the intensity at each pixel, images of the carbon density were obtained. The C-mapping indicated that the section contains an estimated 34 vol. % of carbon.

The bonding state of carbon can be inferred from the x-ray absorption near-edge structure (XANES). Carbon-XANES spectra, shown in Fig. 1, were obtained at four locations on the IDP section, identified as having high carbon concentrations. In most areas the spectra showed three pre-edge resonances, although one region showed no peaks. The three peaks are π^* resonances due to carbon double or triple bonds. At least two distinct phases of carbon were identified.

(1). E. Anders, *Nature* 342, 255 (1989).

(2). G. J. Flynn, *Lunar Planet. Sci.* XXIV, 493 (1993).

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Figure 1. Carbon XANES spectra of four regions on a ultratomed section of an IDP. The spectra have been vertically displaced for clarity.

Phase-retrieval x-ray microscopy via Wigner-distribution deconvolution.

X1A

Henry N. Chapman (SUNY at Stony Brook)

The microdiffraction plane of a scanning transmission x-ray microscope (STXM) contains a mixture of diffraction and holographic information. By collecting a microdiffraction pattern at each point in a scan of a specimen it is possible to phase the patterns, as has been described by Rodenburg and Bates (1). It has been shown that the complete data set (which is equivalently the set of all coherent dark- or bright-field images collected as a function of detection position) is the convolution of the Wigner distribution function (WDF) of the specimen with that of the probe-forming lens. This is the first demonstration of the method using x rays.

Experiments have been carried out at X1A, using the CCD-STXM as previously described (2). The data presented here were recorded at a wavelength of 3.2 nm, using a zone-plate that has a numerical aperture of 0.036 at this wavelength.

A microdiffraction data set from a sample consisting of $0.5\text{-}\mu\text{m}$ latex spheres was collected. The incoherent bright-field image and retrieved phase image are shown in Fig. 1, where (a) represents the incoherent bright-field, measuring the intensity transmission of the specimen and (b) shows retrieved phase image, displayed with black = -2.1 rad , white = 0.7 rad . Scalebar is 1.0 micron. Another data set of a single latex sphere was also collected and deconvolved, and a line from the resulting phase image is plotted in Fig. 2. The theoretical phase is also plotted on this graph. As can be seen, the phase measurement agrees quantitatively with theory. The estimated errors of the measurements are 0.1 radian in phase and 4% in amplitude. However, further analysis has shown that greater accuracy can be achieved (an error of 0.03 radian in phase) by utilising a greater proportion of the vastly overdetermined data set. The result is that the phase of the zone-plate pupil is also determined. Hence the method offers a highly accurate way of measuring x-ray optical constants, gives quantitative microscopic images, and can be used as a very sensitive way to characterise x-ray optics.

(1). J. M. Rodenburg and R. H. T. Bates, *Phil. Trans. R. Soc. Lond. A* 339, 521 (1992).

(2). H. N. Chapman, C. Jacobsen, & S. Williams, *Rev. Sci. Instr.* 66, 1332 (1995).

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Figure 1.

Figure 2. Plot from an image of the retrieved phase of the complex transmission of a single latex sphere. Also shown is the theoretical phase retardation.

DARK-FIELD X-RAY MICROSCOPY OF IMMUNO-GOLD-LABELLED CELLS.

X1A

Henry N. Chapman, Chris Jacobsen, and Jenny Fu (SUNY at Stony Brook)

The methods of immuno-labelling make visible the presence of specific antigens, proteins, genetic sequences, or functions of a cell. With visible-light microscopy, such as confocal fluorescence microscopy, labelled whole cells can be examined at a resolution approaching $0.25\ \mu\text{m}$, whereas electron microscopes can image labelled thin section at much higher resolution. X-ray microscopy bridges the gap between light microscopy and electron microscopy, in that cells can be viewed at resolutions about five times better than the best confocal light microscopes, free of artifacts due to sectioning or dehydration. In x-ray microscopy, dark-field imaging has been shown to be an ideal way of imaging colloidal gold (1). The dense, sub-resolution, colloidal gold particles scatter strongly and can be detected with high contrast in the dark-field mode. Colloidal gold is a common label used in electron microscopy. Thus, the huge literature of well-documented labelling protocols can be applied directly to x-ray microscopy.

Images of immunogold-labelled fibroblasts are shown in Fig. 1. This sample has also been examined in a transmission electron microscope (TEM). Comparison of the STXM and TEM images shows that the DF image is almost entirely due to scattering from the labels whereas the BF image shows contrast mainly due to the absorption by the carbon of the cell. The apparent diameter of a labelled microtubule in both the STXM DF and TEM images is about 60 nm, and labels separated by 70 nm can be easily resolved.

(1) H. N. Chapman, C. Jacobsen, S. Williams, and J. Fu, Ultramicros. (accepted).
Supported by the NSF (Grant No. BIR-941957) and the DoE (Grant No. DE-FG02-89ER60858).

Figure 1. (A) STXM dark-field image, and (B) STXM bright-field image, of a fibroblast labelled with silver-enhanced 10-nm immunogold, attached to the microtubules of the cell. The bright-field image is a map of the absorption, due mostly to carbon, whereas the dark-field image is a map of the scattering, primarily from the label. The cell was prepared by K. Hedberg, University of Oregon.

Inner Shell Spectroscopy and Imaging of a Subbituminous Coal

X1A

G.D.Cody, R.E.Botto (ANL), H.Ade (NCSU), S. Behal, M.Disko (Exxon) and S.Wirick (SUNYSB)

Inner-shell microspectroscopy has been used to provide in-situ microanalysis of organic and inorganic constituents within Wyodak subbituminous coal (APCS No.2). Two specimens were prepared, one loaded with Ca^{2+} and the other rinsed in HCL. Carbon NEXAFS spectroscopy was used to determine the chemical structure of liptinitic and huminitic macerals. Liptinite was characterized by an abundance of aliphatic carbon, evident by the intensity of absorption assigned to the transition from carbon's 1s orbital to a mixed valence/Rydberg state; a low concentration of aromatic carbon, evident by low-intensity absorption associated with a $1s-\pi^*$ transition; and an appreciable quantity of carboxylic functionality, evident through a relatively intense absorption associated with a $1s-\pi^*$ transition due to $\text{C}=\text{O}$. The huminite exhibits fine structure indicative of an abundance of both aromatic and aliphatic carbon. The presence of polyhydroxylated aromatic carbon and carbonyl associated with carboxylic acids is also clearly indicated. In addition to carbonaceous heterogeneities, chlorine-rich inclusions were also identified. These were observed to strongly absorb in the energy range near 270eV corresponding to Cl's 2s absorption edge. The inclusions are anticipated to be inorganic chlorides, precipitates which formed following the rinse in dilute HCL. Imaging and spectroscopy on the calcium's 2p absorption edge reveals that the chloride's cation is not calcium, although calcium is detected in the huminite of the Ca^{2+} loaded coal.

Figure 1. C-NEXAFS spectrum of huminite. Intense bands associated with aromatic, hydroxylated aromatic carbon, and aliphatic carbon are clearly evident.

Figure 2. C-NEXAFS spectrum of liptinite. Note the minimal intensity of the $1s-\pi^*$ absorption band near 285.5eV and the very intense mixed valence/Rydberg absorption band near 288eV.

The Application of Soft X-Ray Microscopy to the In-Situ Analysis of Sporopollenin/Sporinite in a Rank Variable Suite of Organic Rich Sediments	X1A
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G. D. Cody, R. E. Botto (ANL), H. Ade (NCSU), S. Wirick (SUNYSB)

Soft X-Ray imaging and carbon near edge absorption fine structure spectroscopy (C-NEXAFS) has been used for the in-situ analysis of sporinite in a rank variable suite of organic rich sediments extending from recent up to high volatile A bituminous coal. The acquisition of chemically based images (contrast based on the $1s-\pi^*$ transition of unsaturated carbon), reveals a homogeneous chemical structure in the spore exine. C-NEXAFS microanalysis indicates chemical structural evolution in sporopollenin/sporinite with increased maturation. The most significant change in the C-NEXAFS spectrum is an increase in unsaturated carbon, presumably aromatic, with rank. The rate of "aromatization" in sporinite exceeds that of the surrounding vitrinite. Increases in the concentration of unsaturated carbon are compensated by losses of aliphatic and hydroxylated aliphatic carbon components. Carboxyl groups are present in low and variable concentrations. Absorption due to carboxyl persists in the most mature specimen in this series, a high volatile A rank coal. The reactions which drive sporopollenin chemical structural evolution during diagenesis presumably involve dehydration, Diels-Adler cyclo-addition, and dehydrogenation reactions which ultimately lead to a progressively aromatized bio/geopolymer.

Figure 1. The C-NEXAFS spectra of sporinite/sporopollenin from samples A-F. With increasing maturity in the coal samples there is an increase in the intensity of $1s-\pi^*$ near 285 eV indicating either an increase in aromatic or olefinic carbon.

Miscibility of poly(ethylene terephthalate) (PET) and polyarylate (PAR) in PET/PAR polymer blends.	X1A
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D.-J. Liu, S.-C. Lui (Allied Signal), V. Zhuang, H. Ade (NCSU), A. Monisera, J. Marty, and J. Chung (Allied Signal)

We have acquired images and point spectra from PET/PAR polymer blends with different overall compositions (PET/PAR 75/25, PET/PAR 63/37, PET/PAR 50/50). The morphologies of the PET/PAR 75/25 and PET/PAR 50/50 polymer blends are shown in Figure 1. In general, the domains become smaller as the PAR concentration is rising. This suggests that mixing gets facilitated and the two polymers become more miscible at the larger PAR concentrations. Point spectra acquired from the respective phases when compared to model spectra of PET and PAR¹ indicates directly that the PAR gets progressively dissolved in the PET and PAR concentration increases. A careful analysis of the data should allow us to provide a quantitative description as a function of blend composition. This kind of measurement and problem can be uniquely addressed with the X1-STXM, since soft x-ray XANES microscopy can provide the chemical sensitivity and spatial resolution necessary to make observations that go beyond merely mapping of morphology of these blends.

1. H. Ade, A. P. Smith, V. Zhuang, D.-J. Liu, S.-C. Lui et al., this activity report.

2. HA acknowledges support from NSF (NSF Young Investigator Award, DMR-9458060).

Figure 1. X-ray micrographs at a photon energy of 285.3 eV of PET/PAR 75/25 (left) and PET/PAR 50/50 (right).

Morphologies of Ternary Polymer blends studied with X-ray Microscopy	X1A
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D.-J. Liu, S.-C. Lui (Allied Signal), V. Zhuang, H. Ade (NCSU), A. Monisera, J. Marty, and J. Chung (Allied Signal)

X-ray Absorption Near Edge Structure (XANES) microscopy provides direct compositional information at relatively high spatial resolution¹. It might therefore be an invaluable tool to characterize multi-component system, such as ternary polymer blends. Traditionally, conventional microscopies, particular electron microscopy in conjunction with staining methods, are used for the characterization of these materials. Many systems of interest contain however components that have very similar absorption rates for staining agents. It is then impossible to delineate these components. Furthermore, there is also always the danger of inducing artifacts associated with the staining process. We have thus started to investigate a variety of multi-component elastic polymer blends with the X1-STXM. As an example, we show the morphology of a blend of poly(ethylene terephthalate), PET, low density polyethylene, LDPE, and Maleated Kraton as acquired with the X1-STXM in Figure 1. Of particular interest is the distribution of the Kraton, a rubbery component, and more specifically whether the Kraton is also located at the PET/LDPE interface. Careful inspection of the micrographs in Figure 1 clearly suggest that indeed the Kraton has a preference to be also distributed at the PET/LDPE interface, rather than just inside the LDPE domains. The features in the lower right hand corner make this particularly obvious: dark domains are touching each other (Kraton around the LDPE domain) in Figure 1A, while by comparison the LDPE domains are sharply delineated and separated in Figure 1B. The interpretation of electron micrographs of stained samples of this material yielded ambiguous results concerning the distribution of Kraton.

1. H. Ade et al., Science 258, (1992) 972.

2. HA acknowledges support through a NSF Young Investigator Award (DMR-9458060).

Figure 1. Left: Micrograph acquired at 299 eV. Both LDPE and Kraton appear relatively dark. Right: Micrograph acquired near 285 eV. LDPE is very transparent and appears bright.

Development of a Cryo Scanning X-Ray Microscope.	X1A
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J. Maser, C. Jacobsen, A. Kalinovsky, J. Kirz, A. Osanna, S. Wang (SUNY at Stony Brook)

Imaging of biological objects in x-ray microscopes is limited by radiation damage to the sample. This limits the spacial resolution obtainable from these samples and the number of images that can be taken from a specific sample area. The latter is important for spectrally resolved imaging and 3D reconstruction. Cryo electron microscopy has shown improved structural stability of frozen hydrated samples. To take advantage of this, we are currently developing a cryo-scanning transmission x-ray microscope (cryo-STXM) which is designed to image frozen hydrated objects at a temperature of below -160°C . In order to allow us reconstruction of a 3D image of an object, cryo-STXM is designed to allow tilting of the sample in excess of $\pm 60^{\circ}$. Unlike existing x-ray microscopes, the cryo-STXM is designed to be run at a vacuum of $\approx 10^{-8}$ torr. This should allow good thermal insulation of the cold sample from the environment, help to reduce thermal drifts, and lead to acceptably low contamination rates. Also, the absorption of x-rays in air is avoided.

This eliminates image noise due to variations of x-ray absorption in ambient helium and should make it possible to use the full spectral range of the water window for imaging, i.e. wavelength between 2.4 nm and 4.5 nm. Most notably, spectral scans with wavelengths around the nitrogen absorption-edge - at a wavelength of 3.1 nm - should be possible. A first test of the mechanical motions and the detector of cryo-STXM have been performed at X1. Full cryo operation is about to start.

Figure 1. Setup of cryo-STXM. The x-ray beam is perpendicular to the paper plane. The sample is held in the cryo holder (A). An airlock allows change of sample without breaking the vacuum. A stepping-motor driven coarse scanning stage (C) is used for changing between different sample areas, and to switch to an alignment pinhole and a resolution test pattern. High resolution scans of small sample areas are performed by a piezo-driven flexure stage (B).

Structured Latex Particles Characterized by Scanning Transmission X-Ray Microscopy

X1A

Gary Mitchell, Mike Cheatham, Yohannes Chonde, Joan Marshall (The Dow Chemical Company), Harald Ade, and Vera Zhuang (NCSU)

Scanning transmission x-ray microscopy (STXM) at X1A is proving to be a valuable means of characterizing the chemical phase distribution of structured latexes. These materials are made by sequentially adding different monomers to the emulsion during the polymerization reaction [1]. The structured latexes may have a gradient or a layered structure or consist of random domains of different chemistry. Figure 1 shows STXM micrographs of thin sections of hollow latex balls made from styrene and acrylate monomers. One can determine the spatial distribution of phases by obtaining images at different, carefully selected photon energies and comparing the resultant images as shown in Figure 1. Polystyrene has an intense absorption peak at 285.5 eV and finite, non-zero absorption intensity at 286.0 eV, whereas aliphatic acrylates have their first absorption peak near 288.0 eV and essentially no absorption at 286.0 eV [2]. The micrographs suggest that the central spot in the particles consists of the acrylic phase and not the styrene containing phase.

References:

1. J. Vanderhoff, J. Park and S. El-aasser, in "Polymer Latexes", ACS Symposium Series 492, (1992) 272.
2. J. Stohr, "NEAXFS Spectroscopy", Springer Verlag, New York, 1992 p. 208 and 230.

Figure 1. Scanning transmission x-ray micrographs of hollow latexes obtained at x-ray energies of 288.4 eV on the left and 286.0 eV for the image on the right. Each image is 7.5 m wide x 7.6 m high.

Interferential differential phase contrast on X1A STXM

X1A

F. Polack (LURE, Orsay, France), D. Joyeux (IOTA, Orsay, France)

Scanning transmission X-ray microscopes (STXM) normally provide pure absorption images. There is however a growing interest for phase microscopy, mainly for its expected ability to reduce the damages from energy absorption. We have set-up an experiment on the X1A STXM, in order to produce a differential phase contrast. It consists in illuminating the sample with two, mutually coherent close spots, instead of one. They produce in the objective and detector planes, a pattern of several fringes the position of which is sensitive to object phase gradients or steps as shown on figure 1. If the detector is shaped in order to detect the flank of one fringe, the set-up is able to detect phase steps between the spots or phase slopes.

Young slits, with aspect ratio 1/1, are used to produce 2 spots separated by one diffraction radius (0.05 μm). The observed fringe profile is close to the theoretical $\text{Sinc}^2(x)$ modulated cosine profile and the measured 0.8 contrast of the central fringe is in good agreement with the value estimated from beam-line data. In a preliminary experiment (94), images of polyimide slabs, 1.1 μm thick, $\sim 5 \mu\text{m}$ wide, $\sim 9 \mu\text{m}$ spacing were made with and without the phase sensitive detection. Figure 2 shows an average of such image profiles over 90 lines. Due to the strong absorption of the object, the phase effect consist in the small overshoot visible on side b.

In an attempt to visualize pure phase contrast at the wavelengths available with X1A STXM, an object made of polystyrene beads in water was chosen this year. Unfortunately, despite the injection of a large helium flow into the microscope, the absorption of the residual oxygen near K edge was so large that no image could be detected. Nevertheless, a new two-element solid state detector for the fringe shift detection, was successfully tested.

Figure 2. Signal profiles of STXM images of polyimide slabs, 1.1 μm thick, part of a polyimide zone plate (courtesy G. Schmahl, Goettingen) : a) energy transmission (without phase sensitive detection), b) energy and phase signal with phase sensitive detection. Profiles are averaged on 90 image lines.

Figure 1. Fringe shift observed in the detector plane as a phase step was moved through the double focal spot.

Semi-Quantitative Determination of the Lateral Orientation in Kevlar Fibers using X-ray Linear Dichroism Microscopy

X1A

A. P. Smith, H. Ade (NCSU), B. Hsiao and S. Subramoney (DuPont Inc.)

We have obtained the first semi-quantitative determination of the relative lateral orientation of various poly(p-phenylene terephthalamide) Kevlar fiber grades using the technique of x-ray linear dichroism microscopy. Micrographs of thin sections (45 degree with respect to the fiber axis) of these technologically important, high crystallinity fibers exhibit a "butterfly" pattern when imaged a photon energies specific to certain chemical functionalities¹. This pattern is reflecting the average lateral orientation of these groups and shows, for example, that the average phenylene ring planes and carbonyl groups are pointing radially outwards. The observed intensity changes of this pattern reflects the relative degree of orientation between the different fiber grades and correlates with the relative crystallinity of these fibers, even though these parameters are not related (Kevlar 149 is largest and Kevlar 29 is smallest.²)

In order to quantify the lateral orientation, carbon K-edge absorption spectra were acquired from several polar angles within the fiber. The photon absorbance is a function of polar angle due to the radial symmetry of the fibers. The differences in the spectra are ascertained by least squares fitting the spectra to extract peak intensities of the various functional groups. A "molecular orientation parameter" is defined for use here as the difference of the absorbance in the vertical and horizontal locations divided by their sum. Using this measure, we have found values of 0.20 for Kevlar 149, 0.12 for Kevlar 49, and 0.09 for Kevlar 29 for the spectral peak dominated by the carbonyl functionality. After correcting for imperfect linear polarization and the geometry during data acquisition and the unit cell, these numbers will reflect the degree of lateral orientation within the fibers. By considering the orientation parameter values for the inequivalent phenylene rings in Kevlar and assuming the [100] direction of micro-crystallites to be radially outward, we find that the angles between these phenylene rings and the chain backbone are inconsistent with those previously reported.³ We conclude that either the [100] direction is not radially outward, or the angle of specific functional groups in the unit cell are different from those previously determined. Additional data, particularly O-XANES, and a refined analysis will allow us to make this determination.

1. H. Ade and B. Hsiao. *Science* 262, (1993) 1427.

2. H. H. Yang. *Aromatic High Strength Fibers* (Wiley-Interscience Pub., New York, 1989.)

3. M. G. Northolt, *Euro. Polym. J.* 10, (1974) 299.

4. HA is supported by an NSF Young Investigator Award, DMR-9458060, and a DuPont Young Professor Grant.

Micro-chemical Characterization of Methylene Diphenyl Diisocyanate (MDI) based Polyurethane Foams using X-ray Microscopy

X1A

A. P. Smith, H. Ade (NCSU) and E. Rightor (Dow Chemical)

We have utilized XANES microscopy to semi-quantitatively determine the chemical composition of a complex chemical system, a methylene diphenyl diisocyanate (MDI) based polyurethane foam. The formation chemistry of these foams is complex and precipitates form during synthesis which alter the physical properties of the material. In order to devise rational strategies to prevent the formation of these precipitates, knowledge about the composition of the system is required. Conventional means have failed to fully obtain this information in a quantitative manner¹ although the three main constituents of the system are known to be an ethylene based polyol, a urea functionality and a urethane functionality².

We have acquired carbon K-edge absorption spectra from several different precipitates and the surrounding matrix. Two of these spectra are shown in Figure 1 and the differences between the matrix and precipitate are clearly evident. By simulating these spectra with absorption spectra of small molecules with similar chemistry³, an estimate of the chemical composition may be obtained. Utilizing diisopropyl ether, phenyl urea and phenyl urethane as model compounds, this procedure estimates the composition of the matrix to be on average 39% polyol, 24% urethane and 37% urea while the precipitates are composed of on average 20% polyol, 52% urethane and 28% urea functionality.

1. S. G. Urquhart et al., *J. Polym. Sci. B: Polym. Phys.* 33 (1995) 1592.

2. G. Woods, *Flexible Polyurethane Foams* (Allied Science Publishers, NJ, 1982)

3. S. G. Urquhart et al., *J. Polym. Sci. B: Polym. Phys.* 33 (1995) 1603.

4. HA acknowledges support through an NSF Young Investigator Award, DMR-9458060, and by the Dow Chemical Company.

Figure 1. Absorption spectra of the precipitates and matrix in an MDI based polyurethane foam.

XANES Spectroscopy of Polyurethane Model Polymers

X1A

A. P. Smith, H. Ade (NCSSU), and E. Rightor (Dow Chemical)

Previous urethane foam characterization, particularly of mechanically detrimental small precipitates, utilized electron energy loss spectroscopy (EELS) and x-ray absorption near edge structure (XANES) spectroscopy^{1,2}. The interpretation of the acquired data is facilitated by the use of spectra from model polymers and molecular analogues. Due to the intrinsically lower radiation damage and better energy resolution achievable with XANES as compared to EELS, we have acquired spectra of several model polymers of significantly higher quality than previously achieved, thus aiding greatly in data interpretation. Four polymers have been studied, each representing a different aspect of methylene diphenyl diisocyanate (MDI) polyurethane foam chemistry³: (i) polyurea, a model for urea functionalities, (ii) BM, a model of the 'hard' urethane segments, (iii) B0, predominantly a long chain polyether linked by urethane functionalities which models the polyol functionalities, (iv) B2, a combination of BM and B0 serving as a model of the MDI foam itself.

1. S. G. Urquhart et al., J. Polymers. Sci. B: Polymers. Phys. 33 (1995) 1592.
2. A. P. Smith, H. Ade and E. Rightor. 'Micro-chemical Characterization of ...', this activity report.
3. C. P. Christenson et al., J. Polymers. Sci. B: Polym. Phys. 24 (1986) 1401.
4. HA acknowledges support from NSF (NSF Young Investigator Award, DRM-9458060) and the Dow Chemical Company.

Figure 1. XANES Absorption spectra of four polyurethane model polymers.

High resolution Fresnel zone plates for scanning x-ray microscopy

X1A

S. Spector, C. Jacobsen (SUNYSB), and D. Tennant (AT&T)

We have fabricated high resolution Fresnel zone plates for use in the Scanning Transmission X-ray Microscope (STXM) at X1A. A Fresnel zone plate is the principle focusing optic in the STXM and usually determines the spatial resolution that can be achieved by the microscope. A Fresnel zone plate consists of a series of concentric rings or zones and its resolution is approximately equal to the outer zone width. We have fabricated zone plates with outer zone widths as small as 30 nm, and preliminary results indicate improved resolution compared to the 45 nm zone plates used previously. The efficiency of the new zone plates is 4.3% at 3.1 nm; this is less than the theoretical efficiency of 10.5%, but it is still high enough for practical use in the STXM.

The zone plates have been fabricated in up to 180 nm of Ge using a trilayer technique similar to one described previously [1]. The pattern is written using a JEOL JBX-6000FS e-beam lithography system. This machine can deliver 100 pA into a 5 nm spot, but it is not optimized for circular structures. We believe some of the loss in efficiency in our zone plates is due to variations in the line width caused by the current method of drawing circular structures. We are working to improve the method used to draw circular structures by modification of the manufacturer's software.

[1] D. Tennant, et al, J. Vac. Sci. Technol. B 8, 1970 (1990).

Figure 1. Scanning electron micrograph of the 30 nm outer zones of the zone plate.

Figure 2. High resolution x-ray transmission image of a test pattern taken in the STXM at X1A. The image was made using a zone plate with a 30 nm outer zone width.

Autoionization into the $1s^{-1}$ continuum following excitation of doubly excited neutral states in CO and N₂

X1B

B. Kempgens, H.M. Köppe, A. Kivimäki, M. Neeb and A.M. Bradshaw (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin)

A strong energy dependence of the vibrational fine structure on the C 1s and N 1s main photoelectron lines has been observed for CO and N₂ at excitation energies 4-7 eV above the core ionization threshold. The branching ratio of the individual vibrational components changes markedly and higher vibrational quanta are excited compared to spectra measured at a few eV higher photon energy. This behaviour suggests that the $1s^{-1}$ state is not reached by direct photoionization but via an intermediate state. Indeed, for both molecules doubly excited 2h2p states have recently been observed about 4 eV above threshold in high resolution absorption spectra. These neutral states, which are energetically in the continuum, can populate the $1s^{-1}$ final state by valence autoionization. The two-step autoionization process causes the variations in the vibrational fine structure seen in the spectra (a) and (c) of the Figure. The autoionization process competes with the resonant Auger decay of the 2h2p states into ionized valence final states.

Figure 1. The vibrationally resolved C 1s and N 1s main photoelectron lines of CO and N₂ measured at two different excitation energies. The photon energies in (a) and (c), which are 5.2 eV and 6.6 eV, respectively, higher than the core ionization threshold, correspond to the double excitation region in the absorption cross section. Note the enhancement of higher vibrational levels. The photon energies in (b) and (d) correspond to values of 16.6 eV and 23.4 eV, respectively, above threshold and here the vibrational fine structure is less prominent.

Deexcitation Spectroscopy of Rb₁C₆₀

X1B

B.Kessler, L.Baumgarten, J.Lüning, S.Cramm, W.Eberhardt (KFA), and J.E.Fischer (UPenn)

We studied the well-characterized orthorhombic phase of Rb₁C₆₀ [1] by direct photoemission and resonant photoemission using the absorption from the C1s core level into the second unoccupied state (LUMO+1) of the fullerene compound. Figure 1 shows the valence-band region of Rb₁C₆₀ recorded with a photon energy of 396.2 eV. The main peak at a binding energy (BE) of about -15 eV is due to photoemission from the Rb 4p levels. The positions of the features at BEs up to about -10 eV correspond to the occupied bands of C₆₀ (see inset). The emission at the lowest BE of about -2.5 eV is attributed to the highest occupied molecular orbital (HOMO) of C₆₀, the peak at about -4 eV corresponds to the HOMO-1. Both orbitals are π -derived for the undoped fullerenes but may undergo hybridization upon alkali doping.

A comparison of valence-band spectra for different photon energies is given in Figure 2. The contribution of the C1s photoemission with 2nd order photon energy ($-2\text{ eV} < \text{BE} < \text{EF}$) has not been subtracted from the spectra. An intensity enhancement close to $\text{BE} = -4\text{ eV}$ can be observed for photon energies between 285.3 and 285.6 eV. In this photon-energy range a transition from the C1s core level into the second unoccupied state of the C₆₀ (LUMO+1) can take place. This excited state causes a resonant enhancement of the HOMO-1 photoemission by a deexcitation process which cannot be observed off-resonance. A possible resonant intensity increase of the HOMO is hidden by the 2nd order peak, but obviously no dramatic effect can be detected for the other C₆₀ derived features. The contribution of the deexcitation process to the photoemission therefore demonstrates that the LUMO+1 level in Rb₁C₆₀ is not completely delocalized.

[1] Electronic Properties of Novel Materials: Physics and Chemistry of Fullerenes and Derivatives, H.Kuzmany, J.Fink, M.Mehring, S.Roth (eds.), World Scientific, Singapore (1995).

Figure 1. Photoemission spectrum from Rb₁C₆₀; inset: valence bands of pure C₆₀.

Figure 2. Resonant photoemission from Rb₁C₆₀.

Electronic decay spectra of doubly excited neutral states in CO and N₂

X1B

M. Neeb, A. Kivimäki, B. Kempgens, H.M. Köppe and A.M. Bradshaw (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin)

The Auger process has been established as the primary decay mechanism for the core-excited states of low-Z molecules both below and above the ionization threshold. Resonant decay can be studied by selecting one-hole one-particle (1h1p) excited states, while above threshold "normal" Auger decay occurs, originating from a mixture of the main ionized single hole state (1h) as well as of shake-up (2h1p) and doubly ionized shake-off (2h) states etc. Since 2h2p states have recently been identified in the high resolution absorption spectra of CO and N₂ about 4-7 eV above the C 1s and N 1s ionization potentials, we have investigated the resonant decay of these doubly excited neutral species. Their decay spectra are characterized by features at higher kinetic energies than the normal Auger transitions. Moreover, some of the lines are extremely sharp. Based on atomic calculations it can be shown that several of the 2h2p states in N₂ give rise to atomic-like decay features which are caused by dissociation of the core-excited molecule. The decay measurements reveal further doubly excited states at and below the core ionization threshold as it was proposed by Arneberg et al. (Chem. Phys. Lett. 91, 362 (1982)) several years ago. These multi-electron excited states cannot be identified in high resolution absorption spectra, since they are obscured below threshold by the more intense 1h1p core-excited Rydberg states.

Figure 1. Decay spectra of CO and N₂ excited around the C 1s and N 1s ionization thresholds at 296.1 eV and 409.9 eV, respectively. The decay of the doubly excited states above threshold show strong resonant features at 268 eV for CO and at 380 eV for N₂, as can be seen in (b) and (d), respectively. The spectra in (a) and (c) show resonant-enhanced structures which are attributed to the decay of additional 2h2p states immediately below threshold. The leading triple peak structure in all spectra is due to direct photoemission of the outer valence orbitals. The valence photoemission spectra of CO and N₂ are shown at the bottom as dotted lines.

Surface Critical Behavior of the beta1-beta2 Phase Transition in V2H X2A

R. Paniago, P.C. Chow, H. Reichert, S.C. Moss (University of Houston), S. Schmid, T.H. Metzger, J. Peisl (University of Munich), K.S. Liang (Exxon)

We have studied the influence of the surface on the beta1-beta2 phase transition of V2H using depth-resolved grazing incidence X-ray diffraction (GID). This second order transition is characterized by the change of the interstitial occupancy of the hydrogen atoms from ordered to random between (101) planes, which can be determined from the hydrogen-induced distortions of the host lattice. First, using in-lab bulk x-ray diffraction, an effective bulk critical exponent beta was determined to be 0.34 ± 0.04 at the specific concentration of 0.49 (H/V, as determined from hydrogen weight-loss measurements). At a slightly higher concentration prior data yielded $\beta = 0.17$. The present crystal traverses a 2-phase region which in turn may complicate the study of the critical behavior. Our GID results indicate an increase of beta from 0.37 to 0.77 in the near-surface region of the crystal and an ordered phase persisting up to 8 Kelvin above the bulk critical temperature, as opposed to a bulk ordered phase that persists 1.0 Kelvin above the phase boundary. As a signature of the presence of a two-phase region we do not observe critical diffuse scattering. However, the surface does show a distinct disordering behavior compared to the bulk, and similar to an ordinary transition. Since a superficial oxide layer was kept to avoid hydrogen losses on heating, its induced fluctuating interaction constants (quenched surface disorder) at the surface do not modify the overall behavior of the hydrogen ordering. Preliminary data on the ordering kinetics indicate a somewhat sluggish behavior at the surface which is driven by a more rapid bulk ordering. This shows that the ordering process is predominately driven by the bulk.

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Figure 1. Vanishing of the (3/2 0 3/2) superlattice peaks at incidence angle α equal to the critical angle for temperatures below and at Tc.

Figure 2. Double log-plot of the superlattice integrated intensity as T approaches Tc.

The Synthesis of a Novel 2-Dimensional Antimony Sulfide, using Synchrotron Imaging Plate Data $[C_4H_{10}N]_2[Sb_8S_{13}] \cdot 0.15H_2O$ and its Structure Solution

X3A1

K. Tan, J. Parise, Y. Ko (SUNY Stony Brook), and A. Darovsky (SUNY Buffalo)

Recently series of main group sulfide compounds, for example, thioantimonates, thioantimonates and thiogermanates have been synthesized using hydrothermal techniques. Specifically, the thioantimonates show a remarkable variation of stoichiometries and structures. A novel antimony sulfide, $[C_4H_{10}N]_2[Sb_8S_{13}] \cdot 0.15H_2O$ was synthesized hydrothermally and its structure was determined from a small single crystal (20 μm 20 μm 60 μm) using Synchrotron Imaging Plate Data. The new compound consists of centrosymmetric Sb_8S_{13} planar clusters. Each cluster is connected to four others through two edge-sharing and two corner-sharing SbS_3 pyramids, forming an extended sheet. The protonated pyrrolidine molecules reside between the parallel stacked sheets. The structure is triclinic (space group P-1 with $a=6.929(2)$, $b=16.747(2)$, $c=17.976(4)$ Å, $\alpha=94.84(1)$, $\beta=95.41(1)$ and $\gamma=125.28(1)$).

Acknowledgments: Work at X-3a supported under U.S. DOE contract DE-FG02-86ER45231. We thank the National Science Foundation (DMR 94-13003) for support.

[1] Parise, J. B.; Ko, Y. Chem. Mater. 1992, 4, 1446.

[2] Wang, X. Eur J. Solid State Inorg. Chem. 1995, 32, 303

Figure 1. The sheet structure of $[C_4H_{10}N]_2[Sb_8S_{13}] \cdot 0.15H_2O$. Each Sb_8S_{13} cluster is connected to four others through two edge-sharing and two corner-sharing SbS_3 pyramids. The connections between clusters are also made by fused -semicubes. Two crystallographic unique pyrrolidine molecules, which are assumed to be protonated, are within the parallelogram-shaped apertures and between the sheets, which are stacked parallel to $[100]$.

The Use of Imaging Plates for Accurate Electron Density Studies at Helium Temperatures *

X3A1

R. Bolotovskiy, P. Coppens, A. Darovsky and V. Kezerashvili (Chemistry, SUNY at Buffalo, and SUNY X3 beamline at BNL)

Short-wavelength synchrotron radiation, helium cryogenic techniques and the oscillation method, have been combined in electron density studies, using imaging plates as detectors. To test the potential and limitations of imaging plates in accurate work, a simple transition metal complex, chromiumhexamine hexacyanochromium, $Cr(NH_3)_6Cr(CN)_6$ was selected for study. X-rays at wavelengths of 0.656 Å and 0.394 Å are obtained at the sideways X3A1 diffraction station [1]. A specially designed antiscattering device [2] allows use of a cryostat in conjunction with imaging plates. The imaging plate data were reduced using the program HIPPO based on the seed-skewness peak integration method [3]. The electron density analysis was performed by Fourier methods and with the aspherical atom multipole formalism [4]. The deformation density maps clearly show bonding features and illustrate the advances made since the first charge density study with synchrotron radiation, performed ten years ago at CHESS on the same compound [5].

[1] A. Darovsky, I. Meshkovskiy, P. Coppens, J. Synch. Rad. 2, 77 (1995). [2] A. Darovsky, R. Bolotovskiy, P. Coppens, J. Appl. Cryst. 27, 1039 (1994). [3] R. Bolotovskiy, M. A. White, A. Darovsky, P. Coppens, J. Appl. Cryst. 28, 86 (1995). [4] N. K. Hansen, P. Coppens, Acta Cryst. A34, 909 (1978). [5] F. S. Nielsen, P. Lee, P. Coppens, Acta Cryst. B42, 359 (1986).

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The structure of TMA-CuGS-2, (Cu _{0.44} Ge _{0.56} S _{2.23}) ₄ (Ge ₄ S ₈) _{3.6} (CH ₃) ₄ N from Synchrotron/Imaging Plate Data. *	X3A1
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J. B. Parise, K. Tan, Y. Ko, (SUNY, StonyBrook), A. Darovsky (BNL)

Single crystals of (Cu_{0.44}Ge_{0.56}S_{2.23})₄(Ge₄S₈)_{3.6}(CH₃)₄N (TMA-CuGS-2) were synthesized hydrothermally. The structure was determined using data collected from 20 μ m crystals at X-3A1.

This compound consists of Ge₄S₁₀⁴⁻ adamantane clusters, corner-sharing with MS_x units (M = Cu, Ge; x = 3 or 4), forming an open framework with tetramethylammonium cations residing within four intersecting channels. Disorder in the M-sites causes the composition of the framework to deviate from the ideal stoichiometry, Ge_{0.71}M_{0.24}S₂, realized when M = Cu and x = 4. This is consistent with results obtained from electron-probe microanalysis. The structure refinements were carried out in space group I-43d with cell parameter a=20.629(1) Å. Fourteen unique weak reflections of the type hhl, 2h+l=4n2, forbidden in I-43d, were detected in the synchrotron/imaging plate experiment. Trial refinements in space groups R3 and I2₁3 suggest their origin in either weak ordering or multiple scattering effects.

Figure 1.

* Work at Stony Brook supported by NSF grant DMR-93-1003.

Synthesis and Structure of Novel Aurates: SrAu ₂ O ₄ and Bi ₄ Au ₂ O ₉ .	X3A1
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J.-H. Park, K. Tan, J. B. Parise (SUNY Stony Brook), A. Darovsky (X3, BNL)

The new compound SrAu₂O₄ was prepared by solid-state reaction of SrO₂ and Au₂O₃ in a welded gold tube at 10GPa and 1200C using a uniaxial split-sphere high-pressure apparatus (USSA 2000) as described previously. [1] Because of the small size of the single crystals (10 × 10 × 20mm³), synchrotron x-ray diffraction was used to collect data for structural determination and refinement. Two sets of imaging plate data with different exposure times were collected at room temperature. An oscillation angle of 25 degree with 5 degree overlap between consecutive frames, was used for the data collection. SrAu₂O₄ (I4₁/a, a = 6.161(2) Å, c = 10.144(2) Å and Z = 4) is isostructural with CaAu₂O₄. [2] It consists of corner-linked AuO₄ square planes and distorted SrO₈ dodecahedra (Figure 1). The AuO₄ units are stacked in a staggered fashion in columns along [100] and [010] to produce a square-antiprismatic arrangement of oxygens between them. The intersection of the columns form cavities containing the SrO₈ units. Another aurate Bi₄Au₂O₉, also prepared at the same conditions, has been studied using the synchrotron/imaging plate data. It has a basic structure similar to La₄Au₂O₉. [3] Its superstructural properties are under investigation.

Acknowledgements: Work at StonyBrook supported by NSF grant DMR-9413003. (1) Gasparik, T. High Pressure-High Temperature, 1993, 25, 245. (2) Park, J.-H.; Parise, J. B. Chemistry of Materials, 1995, 7, 1055. (3) Ralle, M.; Jansen, M. J. Alloys Comps. 1994, 203, 7-13.

Figure 1. Projection of the structure of SrAu₂O₄ along [100]. The AuO₄ units and Sr ions are represented by the planes and circles.

Pair-density Function Analysis of PEOX/SiO₂ Composite Materials X3A1

H. D. Rosenfeld, R. L. Harlow and I. A. David (DuPont)

It has been our goal to prepare composite materials of an organic polymer and an inorganic glass in which the molecules of each component were intimately entwined within those of the other. Such a structure would be a molecular interpenetrating or semi-interpenetrating network, depending on whether the polymer molecules were cross-linked or linear, respectively, and would consist of only one phase. A combination of poly(ethyloxazoline) (PEOX) with SiO₂ in a ratio of 33/67 appeared to meet the "one phase" criterion when the composite was characterized by a wide variety of techniques. However, in-house wide-angle diffraction scans on composites with varying PEOX/SiO₂ ratios proved difficult to interpret since there was little change in the broad peaks of these amorphous materials.

It was then decided to study this material using the pair-distribution technique to see if we could distinguish a true one-phase composite from a two-phase physical mixture. Wide angle diffraction patterns were collected on beamline X3A1 at a wavelength of 0.6535 Å in a low-resolution mode consisting of a receiving slit and a scintillation counter. Data was collected on four samples: pure SiO₂, pure PEOX, a physically mixed sample of PEOX and SiO₂ in a 33/67 ratio, and the 33/67 PEOX/SiO₂ composite material. Background was measured and appropriately subtracted from each pattern. After further corrections for Compton scattering and absorption effects, the resulting patterns were Fourier transformed to yield the PDF patterns. An analysis of all four patterns quickly showed that the distribution of the densities of the distances between atomic pairs in the 33/67 PEOX/SiO₂ composite corresponded to that calculated for a single phase structure but not to that calculated for a two-phase structure. On the other hand, the distribution derived for the physically mixed composite clearly corresponded to that calculated for a two-phase and not a single-phase structure.

Charge Density Studies Using High Energy Synchrotron Radiation at 20K * X3A1

H. S. Sheu, C. C. Wang, C. R. Lee, Y. Wang (Chem., National Taiwan Univ., Taipei), A. Darovsky, R. Bolotovskiy and P. Coppens (SUNY Buffalo and BNL)

We have performed charge density studies at NSLS, using imaging plates (IP) and a Displex cryostat CT20 equipped with an anti-scatter device¹ at the fixed angle X3A1 station. A wavelength of 0.394 Å from a Si(200) monochromator was used. The reduction on the absorption and the extinction should be apparent. Seventy-one frames of diffraction data are collected on IP for a LiB₃O₅ crystal at 20K, the maximum $\sin\theta/\lambda$ is 1.77 Å⁻¹. A total of 4451 unique observed reflections is resulted after averaging the equivalents, the interset agreement index is 0.051. The "seed-skewness" method² is used for the intensity data processing. Thirty-one frames of data are collected on a Fe(phen)₂(NCS)₂ crystal (0.08x0.08x0.04 mm) at 20K, the data resolution is up to 1.036 Å⁻¹. A total of 4211 unique reflections is yielded after averaging the equivalents, the interset agreement 0.054. One hundred and thirty-five frames of data are collected on a Co(C₄O₄)(H₂O)₂ crystal (0.1x0.1x0.1 mm) at 20K. There is an apparent phase transition between the room temperature and 20K. When the crystal is cooled below 200K, substantial peak broadening is observed. It is still so at 66K. But at 20K, peaks are sharpening, however not as sharp as those at room temperature.

1. A. Darovsky, R. Bolotovskiy and P. Coppens, J. Appl. Cryst., 1994, 27, 1039.

2. R. Bolotovskiy, M. A. White, A. Darovsky and P. Coppens, J. Appl. Cryst., 1995, 28, 86.

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A Novel Antimony Sulfide Templated by Dimethylammonium* X3A1

KEMIN TAN, YOUNGHEE KO, JAEHYUN PARK and JOHN. B. PARISE Dept. of Earth and Space Sciences, SUNYSB, Stonybrook, NY11794 ALEX DAROVSKY SUNY X3 beamline

Hydrothermal synthesis has produced a new open framework antimony sulfide, $[\text{C}_2\text{H}_5\text{N}][\text{Sb}_4\text{S}_7]$. A small single crystal of this compound, $0.020 \times 0.03 \times 0.04\text{mm}$ in size, has been used in the x-ray experiments for structure analysis. Two sets of data were collected with different rotation axes measured at the X-3A1 beamline using imaging plates as area detectors. This was done to ensure a complete set of unique data were collected.

The structure of the sulfide (S.G.: Cmca., Cell parameters: $a = 9.9704(7) \text{ \AA}$, $b = 11.652(2) \text{ \AA}$ and $c = 25.979(3) \text{ \AA}$) consists of inter-locking double chains, which are formed from two Sb_4S_7 single chains through S-S bridges. Protonated dimethylamine molecules reside within double chains' openings, which can be treated as 18-membered rings. The structural building units of this material are very similar to that found in the open framework antimony sulfides templated by piperazinium [1] and enthylenediammonium [2].

[1] Parise, J. B. & Ko, Y. Chem. Mater. 4(1992)1446-1450.

[2] Tan, K., Ko, Y. & Parise, J. B. & Ko, Y. Acta Cryst. C50(1994)1439- 1442

Figure 1. Structure of the antimony sulfide templated by dimethylammonium.

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Draw Induced Crazing in PET Fibers: Temperature Effect X3A2

Paul Harney, Benjamin Chu, Alan Kennedy, Roger Leach (Dept. of Chemistry, SUNY at Stony Brook; DuPont Central Research and Development)

On going study of the morphological changes in fibers by synchrotron x-ray scattering has been enhanced by the design and construction of a miniature draw unit. On-line drawing of fibers is better suited for comparison to industrial processing techniques. This method appears ideal for obtaining the long exposure times necessary for fiber scattering volumes which tend to be small.

Use of the draw unit for SAXS and WAXS experiments has provided better precision of morphological changes as the temperature is raised above the T_g . Between 30°C and 50°C , the typical cross SAXS pattern showed an initial increase in the meridional spike as seen in Fig 1. WAXS data, shown in Fig 2 remained unchanged through these temperatures. At about 60°C , SAXS intensity began to decrease, and was marked by an increase in orientation observed in the WAXS data as evident from an increase in equatorial intensity and corresponding decrease in the meridional intensity. By 70°C little evidence of crazing was seen in the SAXS patterns, and the meridional WAXS peak began to show increased asymmetry. Assuming a baseline of amorphous material for subtraction, the remaining WAXS pattern appeared similar to the mesomorphic form¹ of PET. The formation of the mesomorphic form of PET seemed to correspond with the disappearance of the craze SAXS pattern.

[1] Parravicini, L. Leone, B. Auriemma, F. Guerra, G. Petraccone, V. DiDino, G. Bianchi, R. and Vosa, R. J. Appl. Poly. Sci.52, 875-885 (1994).

Figure 1. Meridional SAXS from PET fibers: Temperature effect.

Figure 2. Meridional WAXS of PET fiber: Temperature effect.

Paul Harney, Benjamin Chu, Alan Kennedy, Roger Leach (Dept. of Chemistry, SU NY at Stony Brook, Stony Brook, NY 11794; DuPont Central Research and Development, Experimental Station, Wilmington, DE)

A miniature draw unit was developed to better reproduce fiber processing and to facilitate further X-ray scattering measurements of this phenomenon. Unlike stretching a fiber, the sample is constantly being replenished in the drawing process. In conjunction with intense synchrotron radiation, this allows for the longer exposure times dictated by the small fiber scattering volume ($\sim 1 \times 10^7 \mu\text{m}^3$ for a 1 mm beam diameter).

WAXS analysis was performed to correlate crystallization with crazing in amorphous PET fibers. A phase transition was observed at the natural draw ratio (NDR), (approximately 2.15). Fig. 1a and b show the meridional and equatorial profiles, respectively, for the WAXS patterns for draw ratios: 2.1 and 2.2.

Draw ratios below the NDR appeared to represent mostly the amorphous phase with minimal organization as observed in DR=2.1. In the strain-hardening region, above the NDR (DR=2.2), the intermediate or mesomorphic phase¹ developed as is typical for drawing PET below the T_g . It, therefore, seems that breakdown of the craze microstructure correlates with the onset of the mesomorphic form during strain hardening.

[1] Parravicini, L. Leone, B. Auriemma, F. Guerra, G. Petraconne, V. DiDino, G. Bianchi, R. and Vosa, R. *J. Appl. Poly. Sci.* 52, 875-885 (1994).

Figure 1. (a, left) Meridional WAXS of PET fiber: DR effect. (b, right) Equatorial WAXS of PET fiber: DR effect.

A.D.Kennedy, B.S.Hsiao, R.A.Leach (DuPont Central Research, Wilmington DE), P.Harney, B.Chu (SUNY at Stony Brook)

Structure change of a drawn, semi-crystalline, 6,6 nylon yarn was monitored in-situ during tensile deformation (1 to 30% strain) at 30 to 225°C on beam-line X3A2. Yarn was continuously taken from a package and strained over heated pins between two rolls moving at different speeds. This steady state process provides continuous sample replenishment and removes time constraints inherent in conventional stretching experiments.

The 2D WAXS patterns were fit to a three phase structure model: crystal + both oriented and isotropic amorphous. Concentration of each was indexed by 2D integration. Substantial crystal melting occurred at 100 to 200°C with a concomitant increase in oriented amorphous content but little change in isotropic amorphous. Crystal melting was reduced at higher strains. Above 200°C, crystal content remains constant but oriented amorphous is converted to isotropic. Observations are strikingly consistent with solid state NMR¹ which shows three levels of N-H mobility above T_g : fixed H-bonds in crystals, both isotropic and a hindered motion in amorphous regions; the fraction of material with isotropic motion increased as temperature approached the melt.

High image quality (ten clear reflections) allowed crystallographic analysis. Collapse of the two strong equatorial reflections into a single peak, the so-called Brill transition, began at about 100°C and was complete at 160. Our analysis confirmed that the transition results from anisotropic crystal thermal expansion. Inter-chain spacing within the H-bonded sheets remains essentially constant while inter-sheet spacing increases sharply, forming a metrically hexagonal structure. Expansion is attributed to CH₂ libration within the crystals^[1].

[1] H.Miura, J.Hirshinger and A.D.English, *Macromolecules*, 1990, 23, 2153 and 2169

Figure 1. Cylindrical co-ordinates for BO2-F18: Calculated model (solid) vs data (dashed).

Figure 2. Crystal index vs temperature.

Valence-specific resonance diffraction with imaging plates applied to the mixed-valence enzyme model complex $\text{Mn}^{\text{IV}}\text{L}(\mu\text{-O})_2(\mu\text{-MeCO}_2)\text{Mn}^{\text{III}}(\text{MeCO}_2)_2$, $\text{L} = 1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane}^*$	X3A2
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V. Kezerashvili, A. Darovsky and P. Coppens (SUNY/Buffalo and BNL)

The title compound (Fig. 1) is a catalytically-active model compound of the catalase enzymes. Single-crystal imaging plate data have been collected at a number of wavelengths in the vicinity of the absorption edge. Given the known structure, the anomalous scattering factor f' of the two Mn atoms can be determined site-specifically. A shift of the absorption edge of Mn(IV) relative to that of Mn(III) is evident in Fig 2. In addition, the pre-edge feature visible in the fluorescence curve is evidently based on a transition at Mn(IV) rather than Mn(III), as only the former shows f' fine structure at the energy of the pre-edge feature (Fig. 2).

The experiment shows that information on the electronic structure of transition metal atoms can be obtained rapidly by resonance scattering. The results have implications for time-resolved studies of electron transfer.

Figure 1.

* Research carried out in part at the National Synchrotron Light Source at Brookhaven National Laboratory which is supported by the US DOE, Div. of Materials Sciences and Div. of Chemical Sciences. The SUNY X3 beamline at NSLS is supported by the Division of Basic Energy Sciences of the US Department of Energy (DE-FG02-86ER45231). Support of this work by the National Science Foundation (CHE9317770) is gratefully acknowledged.

Figure 2.

Self assembly of block copolymer Poly(oxyethylene-oxypropylene-oxyethylene) L64 in <i>o</i> -xylene/water system	X3A2
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Li-Zhi Liu, Vinh-Bao Buu, Benjamin Chu (Department of Chemistry, SUNY at Stony Brook)

In recent years, there have been a number of studies dealing with the Pluronic L64 in aqueous or nonaqueous solvents. However, the behavior of L64 at high concentrations is not often studied. Therefore, at high concentrations, their colloidal behavior is still not very clear.

In our experiments, we selected a total copolymer concentration of $C = 0.617\text{g/mL}$ to study the aggregate structures as a function of water-to-EO molar ratio ($Z = [\text{H}_2\text{O}]/[\text{EO}]$) by synchrotron SAXS at 25°C .

Four solutions with an initial concentration of 0.617g/mL were prepared by dissolving L64 in *o*-xylene. Then calculated amounts of water were added to each sample to get four different water-to-EO molar ratios: 0.9, 1.4, 1.7, 2.1. We annealed the samples for a few days before the SAXS experiments.

The graphs obtained are shown below. For the samples with $Z = 0.9$ and 1.4, the first order peaks are observed but the high order peaks did not appear. For the solutions with $Z = 1.7$ and 2.1, besides the main peaks, the SAXS profiles contain higher order peaks, with the Bragg ratios of $1:4^{1/2}:7^{1/2}$ and $1:3^{1/2}:4^{1/2}:7^{1/2}$ respectively, suggesting that the microstructures formed are hexagonal.

Figure 1. SAXS profiles of L64/Cyclohexanol samples.

SAXS	Study	of	
the Miscible Blends of Semicrystalline Poly(vinylidene fluoride) and Semicrystalline Poly(1,4-Butylene Adipate)			X3A2

Li-Zhi Liu and Benjamin Chu, R. St. John Manley (Dept. of Chemistry, SUNY at Stony Brook; Dept. of Chemistry, McGill University)

The miscibility and phase behavior of mixtures of poly(vinylidene fluoride) (PVF2) and poly(1,4-butylene adipate) (PBA) have been investigated by Manley and coworkers using differential scanning calorimetry and light-scattering techniques. It was concluded that PVF2 and PBA are thermodynamically miscible in the melt. The mixtures exhibit a complicated phase behavior, such as a three-phase morphology in which two different crystalline phases co-exist with an intimately mixed amorphous phase.

Synchrotron SAXS was used to study the three-phase structures at room temperature and two-phase structures at 70°C of the miscible PVF2/PBA blends. With the addition of PBA, the long period of PVF2 increased and the scattered intensity increased enormously, as shown in Figure 1, due to the density change in the amorphous PVF2 lamellae solubilized with PBA. The SAXS curve of the blend with 30% or more PBA also showed a PBA scattering shoulder (or peak) at higher q-ranges (Figure 1 and 2). Based on our results, a three-phase structure model in such miscible crystalline/crystalline polymer blends is being formulated.

Figure 1. SAXS curves of PVF2 (filled triangle) and PBA (filled circle) homopolymers and their blends with 10% (open circle), 20% (open triangle), and 30% (open hexagon) PBA.

Figure 2. SAXS curves of PBA (filled circle) homopolymer and PVF2/PBA blends with 40% (open triangle), 50% (open square), and 60% (open circle) PBA.

SAXS Studies of Surfactant - Cationic Gel Products	X3A2
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E. Sokolov, F. Yeh, B. Chu, S. Starodubtsev, A. Khokhlov (Dept. of Chem., SUNY Stony Brook; Physics Dept., Moscow State University.)

SAXS studies of slightly crosslinked gels of poly-(diallyldimethylammonium chloride - acrylamide) random copolymer cationic gels in aqueous solution have been performed at the X3A2 beamline at NSLS. The gels with various degrees of crosslinking and diallyldimethylammonium chloride (DADMACl) - acryl amide (AAm) contents were studied. Scattering curves are presented in Fig 1. Gels were also exposed to dilute solutions of anionic surfactants - sodium alkyl sulfates. Gel complexes with sodium decyl (SDCS), dodecyl (SDS), tetradecyl (STS), and hexadecyl (SHS) sulfates exhibit crystal-like structures for the gels with high contents of DADMACl. Sodium octyl sulfate complexes showed semicrystalline properties. The d-spacing of the crystals did not depend on the degree of crosslinking, instead it decreased with increasing DADMACl content. Crystal-like structure disappeared below a threshold value for DADMACl content. Formation of crystal-like structures occurred at surfactant concentrations well below saturation in the external phase. When the surfactant concentration exceeded the critical micelle concentration in the external phase the diffraction phenomenon disappeared.

Figure 1. SAXS profiles of plain gels with 1/200 crosslinking ratio.

Figure 2. SAXS profiles of surfactant-gel complexes for various surfactants. Charge density 100%, crosslinking ratio 1/200.

Morphological Changes During Secondary Crystallization and Subsequent Melting in Poly(ether ether ketone) as Studied by Real Time Small Angle X-Ray Scattering

X3A2

Ravi Verma (DuPont and Virginia Tech.), Herve Marand (Virginia Tech.) and Benjamin Hsiao (DuPont)

Poly(aryl ether ether ketone) [PEEK] is a semicrystalline polymer which exhibits the double endothermic melting behavior. A "low endotherm" is observed in a differential scanning calorimetry scan at about 5-15°C above the crystallization temperature in addition to the high endotherm at about 340°C. It is also established that the low endotherm develops linearly with log of crystallization time. We have monitored the development of the low endotherm and subsequent melting via real time small angle X-ray scattering (SAXS) using synchrotron radiations (beamline X3A2). SAXS data was analyzed via a novel combination of the correlation and interface distribution functions. Our analysis indicates that the development of the low endotherm is accompanied by the formation of secondary lamellar stacks. The relative amount of the secondary lamellar stacks is estimated by the normalized height of the first minimum in the interface distribution function (see Figures). Our analysis indicates that the (1) amount of secondary lamellar stacks increases linearly with annealing time during crystallization and (2) decreases substantially at temperatures corresponding to the low endotherm during melting.

This work was supported by the National Science Foundation under DMR 91-2004 93-57512 and also by the DuPont Central Research and Development.

Figure 1. Morphological variables during heating at 2.5°C/min of a PEEK sample isothermally crystallized at 300°C for 1 hr. The total scattering invariant (Q) is plotted against the left abscissa. The height of the first minima ($g(1,x)$) in the interface distribution function is plotted against the right abscissa.

Figure 2. Morphological variables during isothermal melt crystallization and subsequent annealing at 316°C. The height of the first minima is proportional to the relative amount of secondary lamellar stacks in the semicrystalline polymer.

Interaction of Polyelectrolyte Gels of Poly (Diallyldimethylammonium Chloride) with Surfactants

X3A2

Fengji Yeh, and Eugene L. Sokolov, Benjamin Chu (Department of Chemistry, SUNY at Stony Brook, New York 11794-3400)

From fluorescence studies of excimer formation of Sodium Dodecyl Sulfate (SDS) and pyrene in both gel phase and external aqueous phase, structure of surfactant aggregates in a polyelectrolyte network was found to be different from that of micelles in water¹. In order to study the structures inside the gels, small-angle X-ray scattering (SAXS) was used to investigate the polyelectrolyte-surfactant complexes of the SDS and the cationic network of polydiallyldimethylammonium chloride (PDADMACl).

Fig. 1 shows the SAXS profile of PDADMACl gel in the presence of SDS with concentration in the external phase below the SDS critical micelle concentration (cmc). The sharp peaks demonstrate that the SDS molecules form a highly ordered structure inside the gels. Fig. 2 shows the effects of changing the charge contents of the polyelectrolyte gel from 100% charged to neutral. The diffraction peaks of the complex decrease with gel charge content. There is no structure formation observed in neutral gel.

[1] Filippova, O.E.; Makhaeva, E.E.; Starodubtzev, S.G. *Polymer Science* 1992, 34, 602.

Figure 1. SAXS profile of PDADMACl(100%, 1/200) in SDS.

Figure 2. SAXS profile of various charge contents of PDADMACl(1/200) in SDS.

SEARCH FOR STRUCTURAL PHASE TRANSITIONS IN Rb _{2.90} C ₆₀ *	X3B1
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G.M. Bendele, P.W. Stephens (SUNY Stony Brook), and J.E. Fischer (U. Penn)

We have carried out an x-ray powder diffraction study of a phase-pure sample of the superconducting alkali-fulleride Rb₃C₆₀ with measurements at T=20K, 35K, 295K, 460K and 575K. Its structure is well known to be cubic (space group Fm $\bar{3}$ m) with a=14.43Å at room temperature. Rietveld refinements of this model clearly yield unit occupancy for the octahedral Rb site and 95% occupancy for the tetrahedral Rb site resulting in a total stoichiometry of Rb_{2.90}C₆₀.

Given the extremely large thermal B-factor of the octahedral Rb, we have searched for evidence of any off-center displacement of this atom. Refining structural models with different amounts and directions of displacement from the (1/2,0,0) position does not change the quality of fit, as long as the amount of displacement is small enough for the B-factor to remain positive (fig. 1). Since this amount decreases smoothly as T decreases, we conclude that the Rb atom is indeed located in the center of the octahedral site.

Previous ⁸⁷Rb NMR measurements show 3 lines below T=443K, although the structural model has only 2 different Rb sites. We do not see any structural change associated with the disappearance of the third NMR line.

Finally, comparing spectra at T=20K and T=35K our data excludes any structural change associated with the superconducting transition of Rb₃C₆₀ at T_c=29K.

Figure 1. B_{oct} (L, in Å²) & R_{wp} (R, in %) vs. displacement in Å

* Work at the SUNY X3 beamline is supported by the Division of Basic Energy Sciences, U.S. Dept. of Energy (DE-FG0286-ER45231). Research at SUNY is supported by the NSF under grant DMR-92-02529.

TDAE-C ₆₀ : Low-temperature structural studies. *	X3B1
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G.M. Bendele, P.W. Stephens (SUNY Stony Brook), D. Mihailovic, and P. Venturini (Univ. of Ljubljana)

Recent reports [1] have shown differences in AC susceptibility of the organic ferromagnet TDAE-C₆₀ below 20K depending on the thermal history of the sample above 30K. It was suggested [1] that merohedral ordering of the buckyballs in the known monoclinic cell [2] is responsible for this.

We have recorded x-ray powder diffraction patterns of this sample using 1.15Å selected by double Si(111) monochromator and Ge(111) analyzer. Room temperature data shows that the sample contains at least one phase other than the known [2] structure of TDAE-C₆₀. We then compare data with the sample (i) quenched to T=77K and then warmed to T=90K (top of fig. 1) and (ii) slow-cooled over 8 hours to T=90K (bottom of Figure 1).

The peaks that can be assigned to the known [2] structure of TDAE-C₆₀ (indicated by peak markers) show no difference at all. However, there are clear differences in peaks that do not belong to this structure, some highlighted in fig. 1. We conclude that the effects discussed in [1] occur in a phase other than the one known until now. We are planning further studies to investigate the nature of this phase.

[1] D. Mihailovic *et al.*, Science 268, 400, (1995)

[2] P.W. Stephens *et al.*, Nature 355, 331 (1992)

Figure 1. Intensity vs. 2θ

* Work at the SUNY X3 beamline is supported by the Division of Basic Energy Sciences, U.S. Dept. of Energy (DE-FG0286-ER45231). Research at SUNY is supported by the NSF under grant DMR-92-02529.

Structure of C₆₀ polymerized at low pressure. *

X3B1

G.M. Bendele, P.W. Stephens (SUNY Stony Brook), A.M. Rao, P.C. Eklund (Univ. of Kentucky, Lexington), and A. Moravsky (Russian Academy of Sciences)

We have performed x-ray diffraction measurements on a C₆₀ polymer transformed at low pressure. X-ray patterns were collected of the pellet-like sample held both parallel (top of fig. 1, upper) and perpendicular (lower) to the diffraction vector k .

This clearly shows that the sample has an anisotropic structure and that the direction of compression has selected a preferred orientation. Accordingly, we present data collected on samples chopped up (bottom of fig. 1, diamonds). We see that this spectrum is a combination of the reflection and transmission spectra.

We cannot index all peaks in this spectrum to any one phase. However, the three unit cells of the known phases of pressure-transformed C₆₀ [1] do index all peaks. Using the published [1] atom positions we have fitted this spectrum to a mixture of the 3 phases, varying only scale factors. The resulting fit would not be considered good in a true powder experiment, but is sufficient to conclude the three-phase nature of this sample. The fit is the solid line (bottom of fig. 1), with peak markers indicating peak positions for the rhombohedral (R, 20%), orthorhombic (O, 60%) and tetragonal (T, 20%) phases. The uniaxial applied stress evidently forces the fullerene molecules close enough to form bonds at lower applied forces than are seen in experiments with true hydrostatic pressure.

[1] M. Nunez-Regueiro *et al.*, Phys. Rev. Lett. 74, 278 (1995)

Figure 1. Intensity vs. $\sin\theta/\lambda$

* Work at the SUNY X3 beamline is supported by the Division of Basic Energy Sciences, U.S. Dept. of Energy (DE-FG0286-ER45231). Research at SUNY is supported by the NSF under grant DMR-92-02529.

Powder diffraction of alkali:alkaline-earth fullerenes. *

X3B1

G.M. Bendele, P.W. Stephens (SUNY Stony Brook), T. Yildirim (NIST), and J.E. Fischer (U. Penn)

We have studied the phase diagram of $A_xBa_{3-x}C_{60}$ ($A = K, Rb, Cs$) using x-ray powder diffraction. The data was recorded using 0.7 Å selected from Si(111) monochromator and Ge(111) analyzer.

We have found stable phases of ABa_2C_{60} for $A = K, Rb$ and Cs . These phases have the same fcc structure (space group $Fm\bar{3}m$) as A_3C_{60} . The alkali atoms occupy the large octahedral sites at $(1/2, 0, 0)$ with an accordingly large thermal parameter, while Ba occupies the tetrahedral sites at $(1/4, 1/4, 1/4)$ with an indication for slightly less than integer occupancy. Raman spectroscopy shows evidence of a charge transfer of 5 electrons per buckyball and none of these samples are superconductors.

Figure 1 shows a Rietveld refinement ($R_{wp}=9\%$) of this model for $RbBa_2C_{60}$.

Figure 1. Intensity vs. 2θ

* Work at the SUNY X3 beamline is supported by the Division of Basic Energy Sciences, U.S. Dept. of Energy (DE-FG0286-ER45231). Research at SUNY is supported by the NSF under grant DMR-92-02529.

Detection limit for polymorphs in drugs using powder diffraction. * X3B1

R. E. Dinnebier, P. W. Stephens (SUNY Stony Brook), S. Byrn (Purdue Univ.), V. Andronis and G. Zografi (U. Wisconsin, Madison)

The qualitative and quantitative detection of small traces of polymorphs plays a very important role in pharmacology. We have used mixtures of the α and γ phases of the anti-inflammatory drug indomethacin ($C_{19}H_{16}ClNO_4$) as a test case.

First we determined the previously unknown lattice parameters of α -indomethacin as $a = 18.2883(8)\text{\AA}$, $b = 25.3866(6)\text{\AA}$, $c = 5.4927(4)\text{\AA}$, $\beta = 94.592^\circ$. From the extinction rules we can deduce $P2_1$ or $P2_1/m$ as possible space groups. The number of formula units per unit cell is probably 6.

We investigated mixtures of 10, 1, 0.1, 0.01 and 0.00 weight-% α phase in γ . 0.1% α could easily be detected with its five strongest peaks. It is difficult to quantify the detection limit below 0.1%, since the starting γ from which these samples were prepared evidently contained a trace of α . Further work with samples of higher purity is underway. The (120) peak of the α phase and the (010) (0.15% of strongest peaks) peak of the γ phase are shown in the scans below.

Figure 1.

* Work at the SUNY X3 beamline is supported by the Division of Basic Energy Sciences, U.S. Dept. of Energy (DE-FG0286-ER45231). Research at SUNY was supported by the NSF under grant DMR-92-02529.

STRUCTURE OF SODIUM-PARA-HYDROXY-BENZOATE BY POWDER DIFFRACTION * X3B1

R. E. Dinnebier, P. W. Stephens (SUNY Stony Brook), M. Pink, and J. Sieler (Univ. of Leipzig, FRG)

The crystal structure of Sodium Para-Hydroxy-Benzoate $NaC_7H_5O_3$ has been solved *ab initio* from powder data. The lattice parameters in $P2_1$ are $a = 16.0367(1)\text{\AA}$, $b = 5.37604(6)\text{\AA}$, $c = 3.63307(3)\text{\AA}$, $\beta = 92.867(1)^\circ$. There are two formula units in the unit cell.

About 400 peaks were extracted for use in the direct method program SIRPOW with which it was possible to determine the entire structure. Of the two possible space groups, $P2_1$ and $P2_1/m$, only the first allowed a satisfactory fit to all the intensities. The relatively high R_{wp} -factor of 19.0% is due to severe anisotropic micro-strain in the material. The FWHM of neighboring peaks can differ by a factor of up to 3.5. The implementation of a strain model including sufficient refinable parameters in a Rietveld program is under progress.

The structure consists of layers of distorted NaO_6 prisms and phenol rings perpendicular to the layers pointing up and down. The Na-O distances vary between 2.26 and 2.88 $\text{\AA}$. These oxygens are coordinated by 3 Na and 1 O in the form of a distorted tetrahedron. The molecular structure is held together by van der Waals forces between the phenyl groups of different layers and additional H-bridge bonding between the oxygens (O-O distance of 2.94 $\text{\AA}$). The layered structure perpendicular to the a axis is shown in fig. 1.

Figure 1.

* Work at the SUNY X3 beamline is supported by the Division of Basic Energy Sciences, U.S. Dept. of Energy (DE-FG0286-ER45231). Research at SUNY was supported by the NSF under grant DMR-92-02529. Research at UL was supported by the DFG and the Fond der Chemischen Industrie in Germany.

Structures of C_6H_5OA ($A = K, Rb, Cs$) by powder diffraction * X3B1

R. E. Dinnebier, P. W. Stephens (SUNY Stony Brook), M. Pink, and J. Sieler (Univ. of Leipzig, FRG)

The crystal structure of industrially important C_6H_5OK has been solved *ab initio* from powder data. The lattice constants for C_6H_5OK in $Pna2_1$ are $a = 14.1005(1)\text{\AA}$, $b = 17.9126(1)\text{\AA}$, $c = 7.1650(4)\text{\AA}$.

X-ray powder diffraction patterns were recorded using $1.15\text{\AA}$ ($A = K, Rb$) and $0.7\text{\AA}$ ($A = Cs$) from double Si(111) monochromator and Ge(111) analyzer. About 300 peaks were extracted for use in the direct method program SIRPOW with which it was possible to detect the positions of A and some candidate O. In the next stage, we searched for the center of gravity locations of the phenyl rings by replacing them with diffuse pseudo-atoms having the same number of electrons but a rather high temperature factor. It was possible to Rietveld-refine such structures to Bragg-R-factors around 30%. Grid searches on the rigid body orientation of the phenyl ring led to refinable coordinates for all of the non-hydrogen atoms ($R_{wp} = 16.1\%$, $R_F = 7.3\%$ for 855 reflections). C_6H_5ORb and C_6H_5OCs were found to be isostructural.

The very unusual structure provides a flagrant violation of Pauling's rule that atoms of a given type should have similar coordination. Note that one set of potassium atoms sits at the center of an oxygen octahedron, while the others are linked to three oxygens and one phenyl ring.

* Work at SUNY X3 beamline is supported by the Division of Basic Energy Sciences, US Dept. of Energy (DE-FG0286-ER45231). Research at SUNY was supported by the NSF under grant DMR-92-02529. Research at UL was supported by the DFG and the Fond der Chemischen Industrie in Germany.

STRUCTURES OF $C_6H_5OK \cdot 2 C_6H_5OH$ and $C_6H_5OK \cdot 3 C_6H_5OH$ BY POWDER DIFFRACTION X3B1

R.E. Dinnebier, P.W. Stephens (SUNY Stony Brook), M. Pink, J. Sieler (Univ. of Leipzig, FRG), and P. Norby (BNL Chemistry)

The crystal structures of the title compounds have been solved *ab initio* from powder data. X-ray powder diffraction patterns were recorded using $1.15\text{\AA}$ from double Si(111) monochromator and Ge(111) analyzer. Lattice params. etc. below:

n	spgrp	a (Å)	b (Å)	c (Å)	Z	# refined atoms (non-H)
2	Abm2	10.1250(1)	21.2424(3)	7.8982(3)	8	10 3 Pbca
22.7726(3)		25.4494(4)	7.7560(1)	8	29	

The structures were solved using the direct methods program SIRPOW to locate candidate positions of K and O. Then, we searched for the center of gravity of the phenyl rings by replacing them with diffuse pseudo-atoms having the same number of electrons but a high temperature factor. Grid searches on the rigid body orientation of the phenyl ring led to refinable coordinates for all of the non-H atoms. Both structures are based on zig-zag chains (along c) of edge-sharing polyhedra.

Work at the SUNY X3 beamline is supported by the Division of Basic Energy Sciences, U.S. Dept. of Energy (DE-FG0286-ER45231). Research at SUNY was supported by the NSF under grant DMR-92-02529. Research at UL was supported by the DFG and ICDD. PN was supported in part by the Danish Research Council.

Figure 1. $C_6H_5OK \cdot 2 C_6H_5OH$

Figure 2. $C_6H_5OK \cdot 3 C_6H_5OH$

FRUSTRATED PHASE SEPARATION IN THE "INTERMEDIATE" FCC PHASE OF K_1C_{60} . *

X3B1

G. Faigel, G. Bortel, M. Tegze, G. Oszlanyi (Research Inst. for Solid State Physics, Budapest), L. Forro (EPF Lausanne), and P.W. Stephens (SUNY Stony Brook)

There has been an interesting puzzle in the phase diagram of K_1C_{60} . Early DSC and x-ray measurements revealed two distinct fcc phases: a rock-salt structure above 450K and an "intermediate" fcc phase below. However, local probes such as Raman, IR, photoelectron spectroscopy, and NMR revealed clear signatures of phase separation into C_{60} and K_3C_{60} below 450K.

We reconcile this apparent discrepancy with a careful analysis of the x-ray profile in the intermediate state at 300K (Fig. 1)[1]. We find that the phase separation is frustrated, so that the C_{60} lattice is coherent over relatively long distances, but the K ions separate into small K_3C_{60} and K-free C_{60} regions. The former are compressed and the latter expanded relative to phase-pure samples of either, resulting in the suppression of the superconducting transitions temperature and magnetic field exclusion in the K_3C_{60} regions, and the suppression of the orientational ordering transition relative to pure C_{60} .

[1] G. Faigel *et al.*, Phys. Rev. B 52, 3199 (1995).

Figure 1.

* Work at the SUNY X3 beamline is supported by US DoE (DE-FG0286-ER45231), at Budapest by OTKA grants, at Lausanne by the Swiss National Foundation for Scientific Research, and at Stony Brook by the NSF.

Crystal Structure Analyses Using Ab Initio Powder Diffraction Techniques: The Failures

X3B1

R. L. Harlow, Z.-G. Li, N. Herron and E. M. McCarron (DuPont)

There has been a great deal of interest in the determination of crystal structures using ab initio powder diffraction techniques. While the successes of the technique have been well publicized, its failures have, unfortunately, been condemned to eternal darkness. We have recently had a number of failures which we are continuing to investigate in the hopes of eventually understanding why these cases proved so difficult. $HAIF_4$, a potential catalyst in the CFC-substitution program, has yet to be solved. Its powder diffraction pattern is characterized by broad peaks which made the unit cell determination rather difficult. We have used electron diffraction to verify two of the axes and have even attempted to use the 2-D intensity data to solve the structure in projection. We have also obtained a pair-density function (data from X17b) which shows that there may be some unusual Al-Al distances, solid-state Al NMR data which clearly indicates that all of the Al atoms are octahedrally coordinated, neutron diffraction data (HFBR-HRNPd) which essentially has verified the unit cell and symmetry, and acid-base information which suggests that the proton is locked up in some fashion. Despite the intense effort and all of this indirect structural information, we have been unable to solve the structure.

$Mo_2O_5(OMe)_2$, a model compound for interaction of methanol with MoO_3 -type catalysts, is an example of a different type. The unit cell determination appeared to be straightforward despite the fact that the peaks were broad and the location of the Mo atom was readily determined from a Patterson map. Six oxygen atoms were subsequently located around the Mo and even the methyl carbons could be seen. The refinement of this structure gave an R value of 11%, i.e. the fit between the observed and calculated data was very good. Nonetheless, while the structure had some chemically reasonable features, it also had some which were not reasonable: e.g. O-Mo-O angle of 60 deg. A neutron powder diffraction dataset (HNRPD) was collected on a deuterated sample: the model developed from the x-ray data does not fit this pattern at all ($R = 50\%$).

The large peak width is the common feature of the synchrotron patterns of these two compounds. This feature not only makes the process of determining the unit cell more difficult but it also blurs the high-angle peaks apparently making it much more difficult to solve the structure. We are continuing to use electron diffraction techniques in the hopes of obtaining starting structures for these two phases. We would like to solve and refine these two structures in order to understand exactly why they proved to be so problematic.

PROBLEMATIC	STRUCTURE
DETERMINATION OF A SMALL ORGANIC MOLECULE VIA	X3B1
AB INITIO POWDER DIFFRACTION TECHNIQUES.	

R. L. Harlow, Z. Li, W. J. Marshall, K.H. Gardner, N. Herron and P. A. Meenan (DuPont)

There is a small number of important organic compounds which have proven difficult to crystallize in sizes that could be used to determine their structures via single-crystal x-ray diffraction. We have begun a program to solve the structures of these compounds using x-ray powder diffraction data but have encountered a number of difficulties. We have selected the molecule shown below as a good example of a "problem" case. The monoclinic unit cell and the space group, $P2_1/c$, were readily determined from the powder diffraction pattern. However, in spite of the small number of atoms in the asymmetric unit (the molecule sits on an inversion center), direct methods initially failed to solve the structure. Essentially, it was solved by inspecting the unit cell dimensions and inserting the molecule in such a way as to maximize the hydrogen bonding and π -stacking. Even then, the refinement of the structure proceeded rather poorly with bond distances and angles becoming chemically unreasonable. A single crystal was eventually obtained by hydrothermal techniques and showed that the structure obtained from the powder pattern was nearly correct but clearly had sufficiently errors in the atomic positions to be quite worrisome. When the molecular structure was idealized (CERIUS) and its structure constrained in the powder refinement, the position of the molecule was found to be similar to that obtained from the single-crystal study. We are presently exploring the "problems" associated with the powder powder study in hopes of understanding their origin and resolving them for future studies of organic molecules.

Figure 1.

The Structure of PrPdSb via Resonance Scattering	X3B1
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A. Mehta (U. of Nebraska), P. W. Stephens (SUNY Stony Brook), S. K. Malik (TIFR), and K. A. Gschneidner, Jr. (Ames Lab)

The crystal structure of PrPdSb is thought to be composed of triangles of Pr-Pd-Sb. An X-ray powder diffraction pattern was collected at a wavelength of 1.15 Å (upto d of 0.9 Å) in parallel beam diffraction geometry with a double Si(111) incident beam monochromator and Ge(111) analyzer before a Na-I detector. Lattice symmetry was found to be hexagonal with $a = 4.58801(1)$ Å and $c = 7.80300(4)$ Å. The extinction space group symmetry was determined from a tabulation of the observed Bragg reflections. Extinction conditions suggest two possible structures for PrPdSb: one in which Pd and Sb randomly occupy the basal sites of the triangles (disordered structure - $P6_3/mmc$) and the other in which Pd and Sb are ordered ($P6_3mc$).

Refinement of these two structures yield very similar fits ($R_{Bragg} = 9.9\%$ for the disordered structure versus $R_{Bragg} = 10.0\%$ for the ordered structure). The similarity of the fits is not surprising in the light of the fact that x-ray scattering cross section of Pd is very similar to that of Sb.

A second diffraction pattern was collected 20 eV below the Pd K-edge (i.e. at 24.325 KeV) where the scattering contrast between Pd and Sb was enhanced by 5 e due to resonance effects. Refinement of the two structures using resonance data indicated a slight preference for the ordered structure ($R_{Bragg} = 8.8\%$ versus $R_{Bragg} = 9.2\%$). The structural fit was, however, still unsatisfactory so difference Fourier synthesis (DFS) maps were generated to determine the cause of the misfit. The DFS maps show that the basal sites of the Pr-Pd-Sb triangles (i.e. Pd and Sb) are split by 0.3 Å. Using DFS maps in conjunction with Pd-Pd and Sb-Sb distances determined from structures of Pd and Sb metals, a new structure for PrPdSb is proposed. In the new structure, Pd and Sb are ordered in the Pr-Pd-Sb triangles but the triangles themselves are disordered. The disorder can be best represented by a random mixing of two types of Pr-Pd-Sb triangles denoted by the configuration Sb-Pr-Pd and Pd-Pr-Sb in space group $P6_3/mmc$. Refinement of the "locally" ordered structure using the resonance diffraction data yields R_{Bragg} of 7.5%, which is a statistically significant improvement (using Hamilton's R-factor analysis) over both the disordered and long range ordered structures of PrPdSb.

Interface Morphology in Lattice-Mismatched (Si,Ge) Thin Films on Si *	X3B1
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Z. H. Ming, S. Huang, Y. L. Soo and Y. H. Kao, (SUNY at Buffalo), and T. Carns and K. L. Wang (UCLA)

The (Si,Ge) system exhibits a number of superior physical properties over pure Si. A higher carrier mobility has already been achieved, and the possibility of varying the Ge content offers a new degree of freedom to control the lattice mismatch and strain in layered semiconductor structures - *band structure engineering*. We have been studying various $\text{Si}_{1-x}\text{Ge}_x$ thin films grown on Si by molecular beam epitaxy in the past several years. This material also offers an ideal system for the study of fundamental physics concerning epitaxial growth of lattice-mismatched semiconductor layers as well as the interfacial morphology. Interfacial roughness parameters and lattice strain of $\text{Si}_{1-x}\text{Ge}_x$ films with varying thickness epitaxially grown on Si(100) are determined using the techniques of grazing-incidence x-ray scattering (GIXS) and diffraction. Recently, we have discovered the roughness of both the buried interface and sample surface follows a power-law scaling behavior as a function of film thickness with an exponent $\beta = 0.71$ for films below the critical thickness, and it undergoes a large change above the critical thickness. Observation of such a scaling law thus establishes a quantitative correlation between the interfacial roughness and lattice strain, and also allows the prediction of interfacial roughness as a function of film thickness of this compound. Work is in progress to compare the interface morphology determined from STM observations and the physical parameters obtained from x-ray scattering, especially in terms of the lateral and vertical correlation lengths of interfacial roughness, fractal dimensions, and variations of interfacial strain in epilayers grown under different conditions.

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Structural Ordering in InGaAs/GaAs Superlattices *	X3B1
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Z. H. Ming, Y. L. Soo, S. Huang and Y. H. Kao (SUNY at Buffalo), and K. Stair, G. Devane, and C. Choi-Feng (Amoco)

For a pseudomorphic multilayer structure consisting of thin layers of dissimilar semiconductors, it is possible to achieve electronic energy band "tailoring" by a control of strain in the material due to lattice mismatch, and to adjust their electronic and optical properties to suit the needs of device applications. When the layer thickness of the constituent semiconductors exceeds a critical thickness, the strain becomes unstable against lattice relaxation in the layer semiconductors, which usually give rise to disordered structural changes such as formation of misfit dislocations and clusters. However, it was discovered in the InGaAs/GaAs superlattices that *coherent* strain can be partly released in the form of structural ordering in a low dimension. Our x-ray scattering studies have revealed a lateral thickness modulation in the [110] direction with a quasi-period of 400 Å. These x-ray results are also in good agreement with direct observation of spatial variation by high resolution transmission microscopy (HRTEM). The resultant material may thus be viewed as an MBE grown-in array of *quantum wires*. Structural parameters pertaining to the morphology of interfaces and thickness variations are obtained. The interfaces in these superlattices are found to be highly correlated, and the layers all show a high degree of crystallinity. Further work is in progress to assess the underlying physical parameters which are responsible for the formation of one-dimensional microstructures in superlattices by MBE. A control of these growth parameters will be very useful for the preparation of arrays of quantum wires for various applications.

* Research supported in part by DOE under grant DE-FG02-87ER45283. Research carried out in part at the National Synchrotron Light Source at Brookhaven National Laboratory which is supported by the U.S. DOE, Division of Materials Sciences and Division of Chemical Sciences. The SUNY X3 beamline at NSLS is supported by the Division of Basic Energy Sciences of the U.S. Department of Energy (DE-FG02-86ER45231).

COMPARATIVE STRUCTURAL STUDY OF A_1C_{60} (A=K, Rb, Cs) *

X3B1

G. Oszlanyi, G. Bortel, G. Faigel, M. Tegze (Research Institute for Solid State Physics, Budapest), P.W. Stephens (SUNY Stony Brook), and L. Forro (EPF Lausanne, Switzerland)

A general trend is established by comparing the lattice parameters of isostructural A_1C_{60} (A=K, Rb, Cs) polymers. The remarkably large differences of their physical properties (Ref. 1) can be related to the variation in the orthorhombic b lattice parameter through the interchain fullerene separation.

phase	a[Å]	b[Å]	c[Å]
KC ₆₀	9.11	9.95	14.32
RbC ₆₀	9.13	10.11	14.23
CsC ₆₀	9.10	10.21	14.17

Figure 1 shows a Rietveld refinement of CsC₆₀ (with a small fraction of unreacted C₆₀). The structural model is that published in Ref. 2, which was mangled in last years' annual report. The temperature dependence of the unit cell dimensions of K₁C₆₀ is shown in Fig. 2, which clearly supports van der Waals bonding along the orthorhombic b and c axes, and covalent bonding along a, as determined from earlier Rietveld refinements.[2]

[1] F. Bommeli et al., Phys. Rev. B51, 14794 (1995).

[2] P.W. Stephens et al., Nature 370, 636 (1994).

Figure 1.

* Work supported by Hungarian OTKA grants, Swiss Nat'l Foundation for Scientific Research, and US NSF. The SUNY X3 beamline is supported by the US DOE under grant DEFG-0291-ER45231.

Luminescence Yield and X-ray Absorption Spectra in Doped Semiconductor Nanocrystals *

X3B1

Y. L. Soo, Z. H. Ming, S. W. Huang and Y. H. Kao (SUNY at Buffalo), and R. N. Bhargava (Nanocrystals Technology)

Recently it has been discovered that doped semiconductor nanocrystals can exhibit novel optical properties which are not found in their bulk material counterparts. Both the quantum efficiency of photoluminescence (PL) and transition probability are enhanced due to the effects of strong localization of electrons in the small particles. We have started a collaborative program with Dr. R.N. Bhargava who first discovered this effect. This new class of materials is of great interest for studying the fundamental physics in systems of reduced dimensions and also for the development of novel optical devices utilizing the unique enhancement effects. Photoluminescence (PL) and x-ray absorption fine structure (XAFS) measurements are made in various doped semiconductor nanocrystals of ZnS and Y₂O₃ with different size distributions. The dopants studied so far include Mn, Tb, and Eu. The interatomic distances between the impurity and neighboring atoms, coordination number, local disorder, and effective valency determined for the nanocrystals are compared with those in bulk doped-semiconductors. For example, in the case of ZnS:Mn, the Mn ions are found to substitute for the Zn sites in the host ZnS but with significant size-dependent local structural changes. The questions of Mn-cluster formation and presence of Mn impurities on the surface of the nanocrystals are addressed. Near edge x-ray absorption fine structures (NEXAFS) indicate that the effective valency of Mn ions in the nanocrystals is close to +2 with a weak size dependence. These local structures are closely related to the observed novel optical properties. More recently, we have discovered that the PL output is sensitive to the energy of x-rays used to excite the nanocrystals. The PL output can thus be utilized for *site-selective* detection of EXAFS. Owing to its enhanced quantum efficiency and fast response, these nanocrystals are strong candidates for a new type of high-efficiency x-ray detector. Further studies of PL and EXAFS in other types of doped nanocrystals are in progress.

Figure 2.

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X-ray Scattering and Absorption Studies of (In,Mn)As Thin Films on GaAs *	X3B1
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Y. L. Soo, Z. H. Ming, S. Huang and Y. H. Kao (SUNY at Buffalo), M. Tanaka (University of Tokyo), H. Munekata (Tokyo Institute of Technology), and L. L. Chang (Hong Kong University of Science and Technology)

The advent of III-V diluted magnetic semiconductors, first successfully synthesized by Munekata *et al.*, offers enormous opportunities for the development of new electronic and optoelectronic devices in which some characteristic physical properties can be *continuously* tuned by an external magnetic field. For a physical understanding of this new class of materials and in light of this important device potential, we have started a systematic study of the interfacial microstructures and local structures in various $\text{In}_{1-x}\text{Mn}_x\text{As}$ films grown on GaAs by molecular beam epitaxy. The methods of grazing incidence x-ray scattering, x-ray diffraction and extended x-ray absorption fine structure are used, from which the interfacial roughness in the layer structure, changes in lattice constants due to strain and lattice mismatch, local environment surrounding the Mn atoms, coordination number, epilayer thickness, and local disorder are determined. Microstructures in MnAs films prepared with different first-layer growth conditions are compared. Our measurements indicate that the template effects can cause significant differences in the local structures and crystallinity of the MnAs epitaxial layers. Substitution of Mn atoms for the In-sites is found in samples either grown at low substrate temperatures (near 200°C) or with a low Mn concentration (about 1 atomic percent). These results provide the first direct experimental evidence for III-V diluted magnetic semiconductors obtained by substitutional doping of Mn impurities in InAs. Further work is in progress to investigate the possibility of controlled doping in p- and n-type materials and the local structures around various magnetic impurities.

* Research supported in part by DOE under grant DE-FG02-87ER45283. Research carried out in part at the National Synchrotron Light Source at Brookhaven National Laboratory which is supported by the U.S. DOE, Division of Materials Sciences and Division of Chemical Sciences. The SUNY X3 beamline at NSLS is supported by the Division of Basic Energy Sciences of the U.S. Department of Energy (DE-FG02-86ER45231).

STRUCTURE OF PHOTO-POLYMERIZED C_{60} *	X3B1
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P. W. Stephens (SUNY Stony Brook), P. C. Eklund, and A. M. Rao (Univ. of Kentucky, Lexington)

When exposed to ultraviolet or visible light in vacuum, solid films of C_{60} become insoluble, evidently through the formation of inter-fullerene covalent bonds [1]. We have investigated the attendant structural modifications using x-ray diffraction. Films were deposited and exposed to light, and the resulting polymerization monitored with Raman scattering (separately from the x-ray experiments). The results clearly show that the solid C_{60} film retains its fcc structure, but its lattice parameter shrinks continuously with increasing polymerization. We have modeled this process as a random network of two types of springs, representing van der Waals and covalent bonds, respectively. Quantitative analysis is hampered by the (evidently) inhomogeneous light exposure to the rather thick films. Accordingly, we will repeat the experiments with thinner films.

[1] A.M. Rao *et al.*, Science 257, 955 (1993)

Figure 1.

* Work at the SUNY X3 beamline is supported by the Division of Basic Energy Sciences, U.S. Dept. of Energy (DE-FG0286-ER45231). Research at SUNY was supported by the NSF under grant DMR-92-02529, and at UKy by NSF OSR-9452895.

THE MICROABSORPTION CORRECTION IN QUANTITATIVE ANALYSIS. *

X3B1

Peter Stephens (SUNY Stony Brook) and Rani Johnson (East Hampton High School)

In applying powder x-ray diffraction to quantitative analysis of solid mixtures, it is generally necessary to correct the measured intensities for microabsorption, i.e., the different absorption constants for the various constituents of the mixture. While the correction for this effect is well known (Ref. 1), it requires knowledge of the average grain sizes of each component and their absorption constants. Using tunable radiation to vary absorption constants, we can determine the parameters necessary to make the Brindley correction directly, without an independent measurement of particle size.

To demonstrate this technique, we prepared mixtures of NIST Standard Reference Materials: $10 \pm 1\%$ by weight Al_2O_3 in Cr_2O_3 , and collected data at wavelengths of $1.54\text{\AA}$ and $0.7\text{\AA}$. The table below shows that, even for these finely ground powders, the Brindley correction is significant at $\text{Cu K}\alpha$, whereas it is negligible at the shorter wavelength. The advantage of synchrotron radiation for these measurements is clear, in that the resolution is not significantly degraded in using shorter wavelengths.

λ	Absorption Al_2O_3	constant Cr_2O_3	Derived weight fraction Al_2O_3
$1.54\text{\AA}$	126 cm^{-1}	912 cm^{-1}	7.5%
$0.7\text{\AA}$	12	97	9.2%

The results are consistent with the Brindley correction for particle sizes of $\sim 1\mu\text{m}$. Clearly this technique could be extended to direct measurements of the particle sizes by collecting data at several wavelengths.

[1] G.W. Brindley, Phil. Mag. 36, 347 (1945).

* Work at the SUNY X3 beamline is supported by the Division of Basic Energy Sciences, USDoe (DE-FG0286-ER45231). Research at SUNY was supported by the NSF under grant DMR-92-02529.

Kinetic Roughening in Ag Homoepitaxy

X3B2

William C. Elliott (University of Missouri-Columbia) Paul F. Miceli (University of Missouri-Columbia) Teddy Tse (SUNY-Stony Brook) Peter W. Stephens (SUNY-Stony Brook)

We have studied, in situ, the kinetic roughening of the $\text{Ag}(111)$ and $\text{Ag}(100)$ surfaces to relate the height difference correlation function to specific details of surface kinetic mechanisms.^{1,2}

These two orientations have contrasting properties; $\text{Ag}(111)$ growth is dominated by the step-ledge diffusion barrier and is multilayer, whereas the $\text{Ag}(100)$ surface undergoes layer-by-layer growth. X-ray specular reflectivity measurements are used to characterize the surface, allowing the rms roughness to be determined at different stages of growth.

Below 300K for the $\text{Ag}(111)$ surface, we observe a power law exponent consistent with Poisson statistics ($\beta=1/2$); however, diffusion over the step-ledge barrier becomes significant at 400K and the growing surface roughens more slowly, resulting in a smaller exponent. The temperature dependence is in agreement with recent computer simulations³ which studied the effect of a step-ledge diffusion barrier on epitaxial growth. The $\text{Ag}(100)$ surface is observed to have exponents smaller than the $\text{Ag}(111)$ surface.

1. W. C. Elliott, P. F. Miceli, T. Tse and P. W. Stephens, Proceedings of the 4th International Conference on Surface X-ray and Neutron Scattering. To appear in Physica B.

2. P. F. Miceli, W. C. Elliott, T. Tse and P. W. Stephens, to be published.

3. Z. Zhang, J. Detch and H. Metiu, Phys. Rev. B, 48 4972 (1993).

Supporting grants: NSF DMR-9202528, DOE DEFG02-86ER45231, University of Missouri Research Board.

Figure 1.

DOMAIN GROWTH IN THE SUBMONOLAYER EPITAXIAL SYSTEM Pb ON Ni(001) *

X3B2

T. Tse and P.W. Stephens (SUNY Stony Brook)

The problem of domain growth is an interesting question in nonequilibrium statistical mechanics, as well as a problem of enormous practical importance. We have studied the scaling of domain size with coverage in the regime from nucleation to the point where growing domains begin to collide. The experimental realization was the monolayer $c(2 \times 2)$ phase of Pb on Ni(001). Adsorbate diffraction peaks at the Ni(100) position were satisfactorily fitted to a Lorentzian to the $3/2$ power, in accord with Porod's law. We obtained usable data for the range of correlation lengths from 16 to 80 Å. Following theoretical guidance from Family and Meakin[1], we looked for exponential growth of domain size by plotting the logarithm of the inverse peak width vs. coverage in Fig. 1. The data fall equally well on a straight line in a log-log plot with a slope of 2.7, but we are not aware of any models that predict such a large growth exponent. Further details are given in Ref. 2.

1. F. Family and P. Meakin, Phys. Rev. Lett. 61, 428 (1988).
2. T. Tse, P.W. Stephens, and P.J. Eng, J. Phys. Condens. Matter 6, 6111 (1994).

Figure 1.

* Work at the SUNY X3 beamline is supported by the Division of Basic Energy Sciences, U.S. Dept. of Energy (DE-FG0286-ER45231). Research at SUNY was supported by the NSF under grant DMR-92-02529.

ADSORPTION SITES OF Pb ON Ni (001) AND Cu(001) vs. TEMPERATURE *

X3B2

T. Tse and P. W. Stephens (SUNY Stony Brook)

In previous work, we have used the interference between Pb and the Ni surface truncation rod at the (bulk-forbidden) Ni (110) diffraction position to show that, at room temperature, Pb adsorbs on the fourfold hollow sites of Ni (001) even before it forms a detectable monolayer. The initial growth mode at elevated temperatures is quite different, as illustrated in Fig. 1 below. At 70°C and below, Pb atoms up to the $c(2 \times 2)$ monolayer scatter out of phase with the Ni surface. At higher temperatures, some of the Pb atoms scatter in phase with the Ni, although the Pb atoms eventually occupy the fourfold hollow sites. We obtain similar results for Pb on Cu(001) (Fig. 2). The temperature dependence evidently arises from the increased mobility of Pb atoms on the surface leading to greater adsorption on step edges or other pinning sites, and the migration of subsequent atoms to these nucleated islands. The solid curves in the figures are fits to a model described in [1].

- [1] T. Tse, P. W. Stephens, and P. J. Eng, J. Phys. Condens. Matter. 6, 6111 (1994)

Figure 1. Ni(110) intensity vs. Pb coverage

* Work at the SUNY X3 beamline is supported by the Division of Basic Energy Sciences, U.S. Dept. of Energy (DE-FG0286-ER45231). Research at SUNY was supported by the NSF under grant DMR-92-02529.

Figure 2. Cu(110) intensity vs. Pb coverage

Transcriptional initiation: TBP/TFIIA/TATA complex.	Structural analysis of the X4A
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Jim Geiger (Howard Hughes Medical Inst., Yale University MB&B) P. B. Sigler (H HMI Yale University MB&B)

The goal of this project is to investigate structure-function relationships of eukaryotic transcription initiation. For RNA polymerase II, there are a host of general transcription factors that must associate at the promoter with the polymerase before transcription initiation begins. Some are required for the initiation of all genes (TFIID, TFIIIB) *in vivo* and *in vitro*, while some are required on a subset of promoters, or serve to activate transcription, but are not necessary for basal levels of *in vitro* transcription. TFIIA falls in the latter category. An essential gene in yeast, TFIIA counteracts the effects of transcriptional repressors and may be involved in the activity of transcriptional activators. It increases the association of TBP to the TATA box by three orders of magnitude, and extends the TBP footprint on DNA by seven base pairs in the upstream direction.

We have crystallized and produced a preliminary electron density map of a complex of TBP/TFIIA/TATA to 3.0 angstroms resolution using two data sets collected at X25: a derivative where both TFIIA and TBP proteins have been substituted with selenomethionine, and a derivative where only TFIIA has been substituted with selenomethionine. The later data set is also the highest resolution data so far collected on this complex and will be used to refine the structure to 2.8 angstroms resolution. More recently we have conducted a double edge Se/Br MAD experiment at X4A which produced a far superior and interpretable electron density map that is presently being traced.

1. Auble, D. T.; Hahn, S. *Genes Development* 1993, 7, 844-56.

2. Meissner, W.; Holland, R.; Waldschmidt, R.; Seifart, K. H. *Nucleic Acids Research* 1993, 21, 1013-8.

Crystal structure of human interleukin-10 at 1.6Å resolution	X4A
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A. Zdanov, C. Schalk-Hihi, A. Gustchina, and A. Wlodawer (NCI-FCRDC)

Interleukin-10 (IL-10) is a cytokine produced by activated T cells, B cells, keratinocytes, and monocytes. It has been shown to inhibit the synthesis of a number of cytokines, including interferon γ , IL-2, IL-3, tumor necrosis factor and granulocyte-macrophage colony-stimulating factor. Human IL-10 has been shown to exist in solution as a homodimer, composed of two polypeptide chains of 160 amino acids each. The subunits within the dimer are non-covalently associated, although each subunit contains two intra-chain disulfide bonds. Structure of IL-10 at room temperature (RT) has been solved by MIR by using five heavy-atom derivatives [1] and refined at 1.8Å resolution against data collected on RAXIS-IIC image plate system coupled with a RU-200 generator.

We were able to collect diffraction data to 1.5Å resolution at low temperature (LT), 100°K, using synchrotron radiation, beamline X4A. Sigma M-3516 mineral oil was used as a cryoprotectant. A total 91 frames of 1.5° oscillations with exposition time 55 sec. per frame were collected. Crystal to detector distance was 150 mm. The data were processed with the DENZO program package; R_{merge} is 7.2% at 1.5Å resolution. However, since the data in the last resolution shell (1.6Å-1.5Å) were of poor quality, we used in the refinement only data to 1.6Å.

LT data allowed us to locate four extra N-terminal amino acid residues and a number of side chains which were not visible before. We identified 175 "new" water molecules and three ammonium sulfate anions. It is interesting that at LT the unit cell (space group P3₂21) became more "trigonal" $a = b = 69.53\text{Å}$, $c = 70.54\text{Å}$ versus $a = b = 70.27\text{Å}$, $c = 70.31\text{Å}$ at RT. The molecule itself appears to contract slightly at LT, similar to what was found in the studies of the Ribonuclease-A at different temperatures [2]. The overall change in the unit cell volume between room and 100°K temperatures is 1.8% or 5336Å^3 . A detailed paper on LT IL-10 crystal structure is in preparation.

[1] A. Zdanov, C. Schalk-Hihi, A. Gustchina, M. Tsang, J. Weatherbee and A. Wlodawer, *Structure* 3, 591-601(1995).

[2] R.F. Tilton Jr., J.C. Dewan, G.A. Petsko, *Biochemistry*, 31, 2469-2481(1992).

Determination of transient molecular structure for photoinduced reaction intermediates using time-resolved energy dispersive XAS.

X6A

L. Chen (Argonne National Laboratory/University of Chicago)

A time-resolved XAS experiment has been set up at the beamline to study laser induced molecular structural changes using energy dispersive x-ray absorption spectroscopy. A Nd-YAG laser pumped OPO laser system (Spectra Physics) offers a continuously tunable nanosecond laser pulses from 420 to 2000 nm at 10 Hz with a pulse energy around 50mJ at 500 nm is installed at the beamline. This laser is used to illuminate the molecules in order to create excited states or photoreaction intermediates. The laser pulses are synchronized with the diode array detector readout, treating the x-ray pulses as a continuous source. Currently the time-resolution of the measurements is limited to the 5-ms readout time of the detector. As the first experiment, we have tried to detect the triplet state structures of ZnTPP (zinc tetraphenylporphyrin) and ZnOEP (zinc octaethylporphyrin), which have lifetimes of 26 and 56 ms respectively at 77K. Based on previous studies, the molecular structures undergo distortions at the triplet state where the symmetry of the molecules change from D_{4h} to D_{4v} or D₂, this hypothesis is yet to be confirmed. We are now in a process to optimize the experimental conditions and explore other suitable molecular systems to study. The outcome of this study will lead to molecular structure determination with higher time resolution at the third generation synchrotron.

The Transient Redox Kinetics of Vanadium Phosphate: An in situ Dispersive XANES Study

X6A

George Coulston, Richard Harlow (DuPont), Simon R. Bare (Dow), Harold Kung, Kari Birkeland, Greg Bethke (Northwestern), John Quintana, Joe Georgopoulos (DND-CAT), and Peter L. Lee (Argonne)

Butane oxidation to maleic anhydride is the only selective alkane oxidation process currently practiced on a commercial scale. Since its development over 20 years ago, this process has received a great deal of attention from the catalysis community; primarily because of hopes that structure-performance relationships derived for the VPO system would lead to development of catalysts for other alkane oxidations. Despite this interest, many basic questions remain unanswered.

For example, it has long been known that lattice oxygen (as opposed to adsorbed oxygen) plays an important role in the mechanism of butane oxidation, but there have been no reports in the literature providing direct evidence of which oxidation states of vanadium are involved in the reaction. In addition, phosphorus enrichment is known to increase the selectivity of vanadium phosphates for production of maleic anhydride, but the reasons for this effect are still unclear. Our collaborative research program at NSLS-X6A has been directed at answering these two very important questions. In a typical experiment, a catalyst cell with Be windows is used to contain a 150 μ m wafer of catalyst.

A bent Si(111) crystal is used to focus a polychromatic x-ray beam onto the wafer, and the transmitted beam is dispersed onto a multichannel photodiode detector. With this configuration, the complete XAS spectrum can be collected with adequate S/N in 1 sec. The reactor exit is in-line with a mass spectrometer so the production of maleic anhydride can be followed during the experiment. The V K-edge XANES data have been analyzed using conventional curve fitting of the edge and pre-edge features as well as with a factor analytic approach. The latter is particularly well suited for analysis of time resolved data because the entire data set is analyzed at once, and there is no need to normalize the spectra or to use external standards.

In a series of experiments using α_1 -VOPO₄/SiO₂, the reaction gas was cycled between air and butane. At all temperatures studied, the overall rate of reduction was always faster than that for reoxidation of the catalysts, although the initial rate of reoxidation was faster for T<420°C. In the case of a phosphorus enriched sample (P:V=1.95) at 320°C, the rate of reduction increased to 0.016s⁻¹, while the rate of oxidation decreased to 0.01s⁻¹. This suggests that phosphorus may play a role in C-H bond activation, but that it has its largest impact on the process by which lattice oxygen is restored. Furthermore, at all temperatures studied, the maleic production rate, as determined by the mass spectrometer, tracked the decay of the V⁺⁵ component of the catalyst, clearly identifying that component as being required for production of maleic anhydride.

K absorption edge Magnetic Circular X-Ray Dichroism of Fe-Ni alloy.

X6A

K. J. Gofron, C.W. Kimball (NIU), P.Lee, G.Jennings, P. A. Montano (ANL)

Here we describe Magnetic Circular X-ray Dichroism (MCXD) studies of Fe-Ni alloy, using energy dispersive beamline. MCXD provides information on element and orbital specific (partial) spin density of unoccupied states. The XANES spectra show shifts of the absorption edge of the order of 40 meV for Fe and 600 meV for Ni. The MCXD spectra depend strongly on the crystal structure. However, MCXD of the Fe K edge has always a positive peak at the absorption edge in the bcc, fcc, and hcp crystal structures with intensity decreasing with decreasing Fe content. MCXD of elemental Ni K edge has only a negative peak. When Fe is added the MCXD of the Ni K edge develops a positive peak at the absorption edge in the fcc and hcp crystal structures. The MCXD signal of the K edges is of the order of 0.1edge.

Figure 1. MCXD spectra at Fe K edge in alloys.

* This work was supported by the State of Illinois/NIU-HECA and Department of Energy under contract W-31-109-Eng-38

Figure 2. MCXD spectra at Ni K edge in alloys.

MCXD studies of the single crystal of $\text{Nd}_2\text{Fe}_{14}\text{B}$ (001). *

X6A

K. J. Gofron, C. W. Kimball (NIU), P.L. Lee, P. A. Montano (ANL), P. Canfield, and M. J. Kramer (Ames Lab)

The MCXD temperature dependent studies of a single crystal of $\text{Nd}_2\text{Fe}_{14}\text{B}$ have been done across spin reorientation at 120 K. The MCXD allowed us to study magnetic behavior of individual atomic species in a complex material. In these studies we used microfocussing property of the energy dispersive beamline in order to study small samples. The MCXD signal at Nd L_2 absorption edge exhibits a change of about 10% across the reorientation temperature. In the same time the room temperature MCXD at K edge of Fe is three times higher than that for elemental Fe.

Figure 1. MCXD at Nd L_2 for $\text{Nd}_2\text{Fe}_{14}\text{B}$ across spin reorientation temperature.

* This work was supported by the State of Illinois/NIU-HECA and the Department of Energy under contract W-31-109-Eng-38

Figure 2. MCXD at Fe K edge for $\text{Nd}_2\text{Fe}_{14}\text{B}$.

Temperature Dependence of the MCXD at the Gd L_3 edge *

X6A

K. J. Gofron, C. W. Kimball (NIU), P. L. Lee, P. A. Montano, G. Jennings (ANL)

We measured the temperature dependence of the magnetic circular X-ray dichroism (MCXD) effect at the Gd L_3 absorption edge using an energy dispersive beamline. The intensity of MCXD features follows closely the standard magnetization curve. In the ferromagnetic region, well below 290 K, the features do not change appreciably. Above the transition temperature, paramagnetic region, the intensity of the MCXD decrease strongly with temperature but are observable even at the highest studied temperatures, 350 K. The main positive MCXD peak is observed at all studied temperatures from 77 K up to 350 K. The peak persists above the zero field ordering temperature (290 K), this is related to the effect of the magnetic field. However, the main focus of the studies is on the presence of the quadrupolar term observed as a feature below the edge. We find that the quadrupolar peak strength does not change significantly over the whole range of temperatures below the reorientation temperature. Thus the coefficients of the quadrupolar term are not strongly temperature dependent as previously assumed. The quadrupolar peak vanishes slightly above the ordering temperature. In addition, magnetic EXAFS oscillations are observed above the valence band region.

Figure 1. Temperature dependence of MCXD at Gd L_3 edge (center). Main peak height (left) as a function of temperature and the MCXD spectrum at 94 K (right).

* This work was supported by the State of Illinois/NIU-HECA and Department of Energy under contract W-31-109-Eng-38.

MCXD studies at Fe K edge in ordered and disordered Fe₃Pt invar alloy. *

X6A

K. J. Gofron, C. W. Kimball (NIU), P. L. Lee (ANL), C. Yahnke (NIU), G. Jennings, and P. A. Montano (ANL)

We have studied magnetism of Fe₃Pt invar alloy at K edge of Fe. Circularly (greater than 95%) polarized x-rays were incident normal to the sample surfaces. Samples were magnetized perpendicular to the surface with field of 1 T using electromagnet. We observe that the MCXD signal at Fe K edge in Fe₃Pt is twice larger and twice broader in energy than in elemental Fe. The K edge MCXD for Fe in Fe₃Pt exhibits complicated structure of positive and negative peaks which have very different intensities for ordered and disordered phases of Fe₃Pt alloy.

Figure 1. MCXD from cold rolled (disordered), heat treated (ordered) Fe₃Pt and elemental Fe. Below are the corresponding XANES.

* This work was supported by the State of Illinois/NIU-HECA and Department of Energy under contract W-31-109-Eng-38

Simultaneous Multi-wavelength Anomalous Diffraction (SMAD) : An Energy Dispersive Synchrotron Diffraction Method for Macro- molecules *	X6A
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Peter L. Lee (ANL) and Craig M. Ogata (HHMI)

A new synchrotron data acquisition method, Simultaneous Multi-wavelength Anomalous Diffraction (SMAD), employing a variable bandwidth curved crystal monochromator (polychromator) coupled with an energy selecting grid plate has been developed. The preliminary data collected of a myoglobin crystal were performed at the X6A beamline at the National Synchrotron Light Source (NSLS). It has demonstrated the ability to measure reflections at six different wavelengths and their Bijvoet pairs at the same time. On one diffraction image, we record both the dispersive and Bijvoet information from a myoglobin crystal for Multi-wavelength Anomalous Diffraction (MAD) phasing.

DETERMINATION OF METAL-METAL INTERACTIONS AND COORDINATIONS STATES OF A MODEL COMPOUND FOR PHOTOSYNTHESIS	X6B
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L. Chen, M. Wasielewski, W. Svec, K. Huang, P. Montano

Chlorophyll dimers play very important roles in energy and electron transfer in natural photosynthesis. In order to study the dimers in natural photosynthesis, the interactions between the macrocycles in the dimers have been studied via various optical spectroscopies and magnetic resonance via various synthetic model compounds. One of such model compounds is bismetalchlorophyll cyclophane, where two chlorophyll macrocycles are connected via two cyclophane linkages. However, the structural detail of such compounds in solution, distance between the macrocycles, the coordination numbers and their correlation with the photophysical properties of the compounds was not available. We studied the metal-metal interaction and the coordination states of the central metal in covalently linked chlorophyll dimers with different central metal atoms (Zn+2, Ni+2, and Cu+2) using XAS. The metal-metal interaction determines the distance between the two chlorophyll rings. This distance and the coordination state of the central metal atom (square planar, pyramid or octahedral) are correlated to the photophysics of the molecules. We observed a possible metal-metal interaction in bis-zinc-chlorophyll cyclophane in toluene solution with a Zn-Zn distance of 3.5 Angstroms and that interaction disappears when pyridine, a strongly binding ligand, is added into the solution (see Figure 1). This metal-metal interaction, however, was not observed in corresponding Cu and Ni compounds, indicating that the configuration of the dimer is strongly determined by the properties of the central metal ions. The coordination states of the Ni bischlorophylls are strongly dependent on temperature, where the hexa-coordination is observed at the 200K or below, and square-planar and penta-coordination is observed at 290K (see Figure 2). This indicated that the ligands, such as pyridine and pyrazine, can be used as probes for the conformation of the chlorophyll dimers. We are continuing this study to further investigate the conformation and photophysics correlation in these molecules and what we can learn about natural photosynthesis from photophysics of the bischlorophylls.

Figure 1. FT-EXAFS of Zn-bis chlorophyll without and with pyridine in solution at 290K.

Figure 2. XANES of Ni-chlorophyll and bischlorophyll complexes.

* Work is sponsored by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract W-31-109-ENG-38 and the Howard Hughes Medical Institute.

M.K. Durbin, A. Malik, A.G. Richter, R.S. Ghaskadvi, and P. Dutta (Northwestern University), and K.G. Huang (Argonne National Lab)

We used grazing incidence diffraction to study the Langmuir-Blodgett (LB) deposition process. A comparison of the results of X-ray studies of ex-situ LB films¹ and their precursor films on water² demonstrates that there is no obvious correlation between the phase of a monolayer on water and the phase on the solid substrate after deposition. In particular, monolayer films of fatty acids on solid substrates have been generally found to be untilted and hexagonal, even when deposited from a phase which is known to have tilted molecules and a distorted hexagonal (DH) lattice. It is not clear when or how the transition from the phase observed on the liquid to the phase observed on the solid takes place. The change might take place as a function of distance from the water meniscus, or it might occur as a thin layer of water between the monolayer film and the substrate dries. With our in-situ X-ray trough, we could study the film as it was deposited, while the temperature and humidity remained the same. We were able to observe structures similar to those seen on the water surface; in particular we observed distorted hexagonal and tilted phases at low temperatures. Figure 1 (top) shows a contour plot of diffraction data taken from a heneicosanoic acid (C_{21} acid) monolayer on a water subphase (pH=2). Figure 1 (bottom) is data from a C_{21} acid monolayer deposited on a glass substrate. The data from Fig. 2 was taken during deposition (the beam spot was 2mm above the water meniscus). The fact that there are two peaks indicates a DH structure and the fact that one peak is off-plane ($K_z > 0$) indicates that the molecules tilt towards a nearest neighbor. As temperature was increased, the monolayer became hexagonal, as is observed on the water surface as well. However, upon decreasing the temperature, we were not able to recover the original distorted hexagonal phase.

1. M.C. Shih, J.B. Peng, K.G. Huang, and P. Dutta, *Langmuir* 9, 776 (1993)
2. B. Lin, M.C. Shih, T.M. Bohanon, G.E. Ice, and P. Dutta, *Phys. Rev. Lett.* 65, 191 (1990)

Figure 1.

* This work was supported by the U.S. Dept. of Energy grant no DE-FG02-84ER45125.

K. J. Gofron, C. W. Kimball (NIU), P. L. Lee (ANL), C. Yahnke (NIU), P. A. Montano, M. Engbretson (ANL)

We studied element and orbital specific magnetism of the Fe_3Pt invar alloy at the L_3 and L_2 edges of Pt, as well as K edge of Fe. Circularly (60%) polarized x-rays were incident normal to the sample surfaces. The samples were magnetized perpendicular to the surface with a field of 1T. The MCXD signals for the ordered (disordered) alloy are 14% (20%) at L_2 edge and 12% (18%) at L_3 edge. The MCXD signal at the L_3 and L_2 edges of Pt are of opposite sign. The K edge MCXD of Fe exhibits a complicated structure of positive and negative peaks. The L edge results are used to estimate orbital and spin magnetic moments of Pt.

This work is supported by the Department of Energy under contract @-31-109-Eng-38 and NIU-HECA/State of Illinois.

Figure 1. MCXD at L_3 edge of Pt for heat treated (ordered) Fe_3Pt .

Figure 3. MCXD at L_2 edge of Pt for heat treated (ordered) Fe_3Pt .

Figure 2. MCXD at L_3 edge of Pt for cold rolled (disordered) Fe_3Pt .

Figure 4. MCXD at L_2 edge of Pt for cold rolled (disordered) Fe_3Pt .

X-ray diffraction studies of non-sulphur self assembled monolayers	X6B
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A. Malik, M.K.Durbin, A.G.Richter, D.J.Campbell, C.A.Mirkin, P.Dutta (Northwestern Univ.) and P.Lee (ANL)

Spontaneously adsorbed monolayers have received much attention for their potential in tailoring surface properties for a variety of applications. Some adsorbate molecules not only form chemical bonds with surfaces but also self-organize into highly ordered structures referred to as self-assembled monolayers (SAM). We and other groups have deposited SAMs of thiols on Au(111) and studied their structures by in-plane X-ray diffraction and AFM. We have analyzed SAMs of azobenzene- and fullerene-terminated alkanethiols by these techniques.

The chemical nature of the thiol-Au interaction has not yet been elucidated. Many feel that the nature of surface attachment involves an Au-thiolate bond, but others have postulated that the sulfur atoms dimerize on the surface to form disulfide-like structures. Many questions remain concerning the relative importance of adsorbate-surface interactions, intermolecular interactions, and kinetic barriers to surface mobility. To probe this issue we have synthesized octadecaneselenol and created SAMs of these molecules on Au(111). Preliminary results indicate that the structure of these films are somewhat different than that of dodecaneselenol. We find that the adsorbates form a hexagonal structure, rotated 30° from the Au(111) lattice, with nearest neighbor spacing of $5.7\text{\AA}$. A radial scan along the $R30^\circ$ direction is shown in figure 1a. The film thickness was estimated to be $\sim 20\text{\AA}$ from the rod scan (figure 1b). By comparing the annealing properties of these monolayers to that of octadecanethiol SAMs we can learn more about the relative strengths of surface-adsorbate interactions and the relative barrier associated with site-to site exchange.

Figure 1.

Effect of the cation on the structure of fatty acid salt Langmuir-Blodgett films	X6B
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A. Malik, M. K. Durbin, A. G. Richter P. Dutta (Northwestern University), P. Lee and K. Huang (Argonne National Laboratory)

Using surface x-ray diffraction, we have studied Langmuir-Blodgett films of fatty acid salts containing lead, cadmium and calcium cations. We find that both the in-plane and off-plane structures of these films change as a function of the cation present. Both the lead stearate and cadmium stearate multilayers have a distorted hexagonal (centered rectangle) in-plane unit cell. In contrast the calcium arachidate multilayers have a triclinic structure (triangular unit cell with all sides of different lengths). The structure normal to plane is also very different in these systems. While the lead samples show long range positional correlation along the surface normal direction (at least up to 4 monolayers), the correlation only extends to two monolayers in the cadmium samples. In the calcium samples there is no correlation between layers.

Radial scans for the three kinds of multilayers studied are shown in figure 1. The two peaks for the lead stearate film correspond to rectangular unit cell dimensions $a=7.33\text{\AA}$ and $b=4.98\text{\AA}$, while the cadmium stearate peaks correspond to $a=7.57\text{\AA}$ and $b=4.84\text{\AA}$. The area per molecule is $\sim 18\text{\AA}^2$ in both cases. The three peaks in the calcium data correspond to unit cell dimensions $a=4.77\text{\AA}$, $b=4.45\text{\AA}$, $c=5.11\text{\AA}$. The area per molecule in this system is $19.57\text{\AA}^2$.

The rod scans at the $1.53\text{\AA}^{-1}$ peak for the three systems are shown in figure 2. From the width of these peaks we estimate the correlation lengths in the surface normal direction to be $100\text{\AA}$, $50\text{\AA}$ and $25\text{\AA}$ for lead, cadmium and calcium multilayers. These correspond to 4 layers, 2 layers and 1 layer respectively. The tilt angle of the chains is $8-9^\circ$ in all three cases.

1) A. Malik, M.K. Durbin, A.G. Richter, K. Huang and P. Dutta, *Phys. Rev B* 52, 654 2) A. Malik, M.K. Durbin, A.G. Richter, K. Huang and P. Dutta, *Thin Solid Films* in press.

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Figure 1. Radial scans for a 5 layered lead stearate, 5 layered cadmium stearate and 6 layered calcium arachidate films.

Figure 2. Rod scans at the $k_{xy}=1.53\text{\AA}^{-1}$ peak for the three systems.

Incipient stage formation of porous silicon *

X6B

H. You, K. Huang, and S.S. Yoo, Z. Nagy (ANL)

It has been widely recognized that porous silicon or porous semiconductors in general are potentially very important materials for future industrial applications. Their main characteristic for potential applications is luminescence at visible ranges. In addition they can easily be manufactured with or into the existing silicon-based electronic devices with anodic dissolution technique. However, In spite that the wide recognition of importance of the materials and intense research of the materials a relatively little attention is given to and little is known about how the anodic dissolution process initiate the formation of the pores at the interface and proceed to the deeper into the samples. This motivated us to perform the *in-situ* x-ray scattering investigation of solution/silicon single crystal interfaces.

In this study, we examined pore formation at the surface of p-type silicon with a resistance of 0.015 Ω/cm . $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{O}=1:1:2$ solution was used and current densities were varied between 10 mA/cm^2 to 200 mA/cm^2 .

An example set of x-ray reflectivity scans is shown in Fig. 1. The top most scan is the scan for a fresh sample surface before dissolution begins. The surface oxide has been removed by the solution leaving the bare silicon (100) surface exposed to the solution. All the reflectivity scans are linear in the log-log scale at large angles. In addition, the slope of the reflectivity changes initially but does not after a few successive dissolutions. On the other hand, the critical angle, above which the reflectivity starts significantly deviates from a constant value, gradually but persistently decreases throughout the entire set of successive dissolutions. The density estimated from the critical angle of the last scan is as small as 40% of the original silicon density. From this observation the process of anodic dissolution in forming porous silicon favors a pore shape which is cylindrically symmetric and the radius changes with a power-law regardless of the pore density or length. A theoretical understanding of this phenomena will be important in any attempt to modeling of the anodic dissolution.

Figure 1. A series of x-ray reflectivity scans made after successive dissolutions of silicon. The scans are vertically offset for clarity.

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Structure of "BaTa_{N2.1}?₁" from a combination of x-ray and neutron data *

X7A

V. Balbarin, F. DiSalvo (Cornell), H. Yamane (Sendai) J. Parise (StonyBrook)

The title phase was prepared from the reaction of a pressed pellet of nitrated barium and tantalum (V) nitride in a 1:1 metals ratio at 1400 °C for 3 hrs under a blanket of clean nitrogen gas. Chemical analysis performed on the fine, purple powder returned 8.55% N and 52.82% Ta by mass; at that time insufficient sample was available to allow an analysis for Ba. The analysis suggests the stoichiometry BaTa_{N2.1}, normalized to 1Ta.

The x-ray diffraction data, collected at X-7A at $\lambda=0.69827(1)$ Å using a position sensitive detector, Ge(111) monochromator, and sample in a 0.3mm dia. capillary, could be indexed on the basis of a hexagonal unit cell. The data are consistent with preliminary evaluations of the sample at Cornell; $a=6.03$ and $c=10.11$ Å. The structure was solved using the x-ray data and Patterson techniques in space group $P6_3/\text{mmc}$ and was confirmed to be similar to the high temperature form of the hexagonal perovskite BaMnO_{3- δ} .

Further refinement was carried out using a set of neutron powder diffraction data collected at room temperature at the HFBR. The refined model can be summarized as follows: BaTa_{N2.1}, $a=6.0274(4)$, $10.1055(7)$ Å; $P6_3/\text{mmc}$; Ta(1) at site 4f ($1/3$, $2/3$, $-0.099(1)$) Ba(1) at site 2d ($1/3$, $2/3$, $1/4$) Ba(2) at site 4e (0, 0, $0.0446(8)$) with occupancy 0.5 N(1) at site 6g (0, $1/2$, 0) with occupancy 0.92(1) N(2) at site 6h ($0.795(1)$, $0.590(1)$, $1/4$ with occupancy 0.48(1))

The displacement parameter for the sites occupied by metals was refined to a value of $0.022(1)$ Å²; for the sites occupied by nitrogens it was fixed at 0.02 Å². The refined values of the occupancies for the N-composition is close to that expected from the chemical analysis - N_{2.1} per Ta site. The distribution of vacancies in the hexagonal perovskite structure is not random however, being concentrated in the N2 site.

* This work was supported by NSF Grant No. DMR-93-1003.

High Pressure and Low Temperature Study of the LTO to LTT Phase Transition in $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$

X7A

M.K. Crawford, R.L. Harlow, E.M. McCarron (DuPont); S.W. Tozer (NHFML, Florida); D.E. Cox (BNL)

We have performed a high pressure, low temperature x-ray diffraction study of the LTO to LTT structural transition in $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$. This phase transition leads to a drastic suppression of superconductivity which is not yet understood. The reported partial restoration of superconductivity under pressure stimulated our study. The structural work was performed using a Merrill-Bassett diamond anvil cell with a 4:1 methanol to ethanol pressure medium. The hydrostatic nature of this medium is illustrated by the diffraction pattern shown in Figure 1. The diffraction linewidths are limited by the position sensitive detector resolution of 0.05 degrees. Measurements at a number of temperatures and pressures suggest that pressure first stabilizes a Pccn low temperature phase. Higher pressures lead to the I4/mmm high temperature phase becoming stable at all temperatures from 300 K to 15 K.

Figure 1.

Study of local atomic order in Pd-Ni-P glasses using resonant x-ray diffraction *

X7A

W. Dmowski and T. Egami (U. Penn.), Y. He and R. Schwarz (os Alamos)

We have studied short range atomic order of three $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ metallic glasses, annealed at different temperatures, by resonant x-ray scattering at the Pd K_α absorption edge. Using the energy dependence of the atomic scattering factor we obtained total and differential structure factor and then by Fourier transform, differential pair distribution function. The Pd differential pair distribution function describes distribution of atoms in the structure with the Pd atom in the origin and allows to study changes in environment of this atom. We examined quantitatively many experimental factors affecting experiment near the absorption edge like energy dependence of f and proper selection of energy windows monitored by detector to account for fluorescence and Compton scattering. We measured the ratio of K_α/K_β above the edge to correct for K_α fluorescence. We determined, frequently neglected, polarization of the primary beam. Figures 1 shows obtained differential structure factor correctly normalized at high Q . Figure 2 presents average (solid line) and differential pair distribution function.

Results show that P-Ni and P-Pd form shortest distances in the structure. The annealing of the glass at high temperature leads to short range ordering of P atoms which may be responsible for the observed embrittlement.

Figure 1. Differential structure factor obtained at Pd K_α edge.

Figure 2. Average (solid line) and differential pair distribution functions for Pd-Ni-P metallic glass obtained at the Pd absorption edge.

* The work at U. of Penna. was supported by the NSF Grant DMR9120688.

W.Dmowski, S.Fu and T.Egami (Univ. of Penn),

One of the experimental difficulties we encounter in carrying out the surface x-ray scattering measurement is that the scattered intensity tends to be very low, since the scattering volume is small and the Bragg peaks are spread normal to the surface forming rods. Accordingly a linear detector is often used in order to achieve parallel photon counting. An alternative, and sometimes superior, method to overcome this problem is to use the energy dispersive x-ray diffraction technique (EDXD). This method uses a white radiation source, and the structural information is obtained by the spectroscopy of the diffracted x-rays measured at a fixed diffraction angle. The spectrum of the diffracted rays is obtained by the use of a solid state semiconductor detector, such as an intrinsic Ge or Li-drifted Si detector, combined with a multi-channel pulse height analyzer (MCA). Using the EDXD method at a grazing angle incidence, in the evanescent wave regime, we studied the atomic structure of ceria (CeO_2) overlayers deposited on the (001) surface of a cubic Yttrium stabilized zirconia (YSZ, $\text{ZrO}_2/\text{Y}_2\text{O}_3$) single crystal. Figure 1 presents a spectrum stored in the MCA that was obtained at $2\theta=26.13$ degrees with the sample in the [1 0 0] direction aligned along the scattering vector. The rection aligned along the scattering vector. The incident and final angles (the angles the incident incident and scattered beams make with the surface of the sample), ai and af, were set above the critical scattering angle. The well defined diffraction pattern from the CeO_2 overlayer indicates that it forms an oriented epitaxial thin film on the zirconia crystal. In this work we have demonstrated that the energy dispersive mode can be successfully used in surface diffraction studies. We were able to observe characteristic features such as the transmissivity and truncation effects on the diffracted intensity. The main advantage of using the energy dispersive mode is high intensity of the scattered x-rays. This allows us to collect data fast and from even smaller scattering volumes. Additionally a family of Bragg diffraction peaks that line up in the same direction can be observed at once. Furthermore, monitoring the fluorescence from various elements can be used to study the concentration depth profile.

Figure 1. Diffraction pattern in energy dispersive mode from the surface overlayer of CeO_2 and single crystal zirconia substrate.

* Supported by National Science Foundation. The work at University of Pennsylvania was supported by the NSF Grant DMR91 20688.

W.Dmowski, D.Louca, T.Egami (U.Penn), D.Kelly and I.Schuller (UCSD)

Fe-Cr multilayers exhibit giant magnetoresistance effect which depends strongly on the preparation conditions. It is observed that GMR effect can be significantly enhanced, up to 300%, by increasing Ar pressure, from 4 to 12 mTorr, during dc sputtering while other parameters are kept constant. There are many studies indicating the role of the interfacial structure on the magnetoresistance effect. To elucidate this point we have performed x-ray diffraction study of three $[\text{Fe}(30\text{\AA})/\text{Cr}(12\text{\AA})]_{10}$ superlattices which had been sputtered in 4, 7, and 10 mTorr of Ar. We used position sensitive detector in horizontal setup to collect simultaneously specular scattering intensity (Q_z perpendicular to the film) and off-specular intensity with Q_y parallel to the plane of the sample. This technique [1] allows to study the effect of the in-plane disorder such as interface roughness or defects at various length scales. In conventional low angle diffraction analysis the effect of interdiffusion or intermixing cannot be separated from the interface roughness. From our study we found that with increasing Ar pressure, there are changes at the interface at three different length scales. The height-height fluctuation function shown in the Fig. 1, is a two-dimensional Fourier transform of the intensity in the Q_x - Q_y plane and describes interface roughness. It shows that at large lateral spacing interface roughness is increasing with Ar pressure. This effect is likely to affect magnetization process. However, at short lengths interface becomes smoother which may lead to the increased electron mean free path. From the integrated in the Q_x - Q_y plane intensity we were able to deduct that there was more interface inter diffusion with higher Ar pressure. Intermixing at the interface can randomize spin dependent scattering potential which would lead to bigger magnetoresistance effect.

1. X. Yan and T. Egami, Phys. Rev. B 47, 2362 (1993)

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Cu⁺ and Fe³⁺ occupancy in Cu_{0.5}Fe_{2.5}O₄

X7A

T. T. Eagen (Alfred U.), D.E. Cox (BNL), S. Dattaguru, and R.L. Snyder (Alfred U.)

A copper ferrite sample (Cu_{0.5}Fe_{2.5}O₄) was processed from CuO and Fe₂O₃. These two compounds were taken in stoichiometry, calcined initially at 950 °C, ball milled, sieved to -325 mesh, heated to 1350 °C in a platinum crucible, and then rapidly quenched into motor oil which was being simultaneously stirred. An initial literature survey indicated that the crystal system was cubic [1], the space group was Fd3m [2], and the oxygen site and lattice parameter were 0.388 and 8.413(3) Å. The sample was run on the X7A beam line at Brookhaven National Laboratory. Three runs were performed using capillary samples at three separate wavelengths, 1.7440 Å, 1.3802 Å, and 1.5000 Å. The powder patterns were then refined in a two-step process (profile fitting followed by structural refinement) with PROFPV (version 3.2 by Toby and D.E.Cox, 1989). Absorption correction was obtained using ABS (VAX program at BNL, 1995). The refined lattice parameter and ion occupancies for the 1.7440 Å pattern were determined to be 8.41550(3) Å and [Cu_{0.253(4)}Fe_{0.747(4)}][Cu_{0.246(4)}Fe_{1.754(4)}]O₄. The intensity R-factor of the refinement was 2.94, the weighted R-factor was 4.83, and the residual was 4.95, as indicated by the profile fit in Figure 1.

[1] E. Prince, and A. G. Treuting, Acta Crystallographica, 9, 1025 (1956).

[2] N. F. M. Henry, and K. Lonsdale, International Tables for X-Ray Crystallography, Vol. I, the Kynoch Press, 340 (1965).

[3] J. Mexmain, Ann Chim, Centre Industriel'Eveux, 297 (1971).

Figure 1. The experimental data ($\lambda=1.7440\text{\AA}$) and a Rietvelt fit of the profile.

PHASE IDENTIFICATION IN GAS-ATOMIZED RE₂Fe₁₄B AL-
LOYS *

X7A

L. Henderson Lewis (BNL), C. H. Sellers (INEL), V. Panchanathan (Magnequench)

The process of inert-gas atomization (IGA) is being explored as a method to produce precursor powders based on the RE₂Fe₁₄B composition for the formation of isotropic bonded magnets. IGA has several advantages over the conventional melt-quenching method: it can produce a large quantity of powder in one step, and it has the potential to be significantly more economical. Initial experiments, however, have proven that the IGA starting ingot composition must be strongly enriched in both rare-earth and boron contents in order to obtain magnetic properties comparable to the conventional bonded magnets. We present here results obtained by x-ray diffraction performed on various powder size fractions of both as-quenched and annealed alloys produced by the IGA process to determine the identity of the impurity phases present and the degree of crystallinity of the primary RE₂Fe₁₄B phase.

X-ray diffraction patterns were obtained in air at room temperature in the range $10^\circ \leq 2\theta \leq 40^\circ$ with wavelengths in the range 0.9 Å - 1.1 Å on samples made of commercial grade alloys with the following nominal compositions:

Fe₁₄(Nd_{0.98}Dy_{0.01}Pr_{0.01})_{2.93}(B_{0.92}Al_{0.08})_{1.33} (Batch 434-2);

Fe₁₄(Nd_{0.92}Dy_{0.07}Pr_{0.01})_{2.90}(B_{0.96}Al_{0.4})_{1.32} (Batch 435-2);

and Fe₁₄(Nd_{0.93}Dy_{0.07})_{2.64}B_{1.28} (Batch 447). Each sample was divided into various size fractions from less than 5 mm to more than 150 mm. The following results were obtained:

1). All size fractions consist overwhelmingly of the well-crystallized RE₂Fe₁₄B phase, with no significant amorphous component. The background signals of the smaller, unannealed samples are always higher than that of their larger or annealed counterparts; additionally, the peak widths are always smaller for the larger and/or annealed size fractions.

2). The amounts of impurity phases are very small, but they are often unidentifiable. This is not a surprising result because the highly non-equilibrium nature of the IGA process would be expected to produce metastable phases.

3). When the impurity phases could be identified it was found that the larger size fractions invariably contained a-Fe, an undesirable product in the formation of permanent magnets. Upon annealing it was consistently found that the intensity of the a-Fe signal decreased while that of the g-Fe₂O₃ signal increased, indicative of iron oxidation in low-oxygen environments. Other impurities were found to be hexagonal RE₂O₃ and a-Fe₂O₃.

4). Least-squares determinations of lattice parameters indicate that the nature of the 2-14-1 phase differs with both particle size and annealing. In specific, it is found that the c-parameter of unannealed portions of Batch 435-2 decrease smoothly as particle size increases, a result that we have interpreted as indicative of a segregation of Dy to the larger-sized particles. Additionally, it is consistently found that the c-parameters decrease upon annealing.

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C.J. Howard, M.M. Elcombe (ANSTO), S.J. Campbell (ADFA) and D.E. Cox (BNL)

The synchrotron work reported here was undertaken in support of a neutron diffraction study of the crystal structure of (nominal) Zr_2NiD_5 .

The initial measurements were made at room temperature. The first was made with the sample in a 0.45 mm capillary using 0.08 nm X-rays, the second was from a flat plate sample at wavelength 0.15 nm, and the third from a flat plate sample prepared after sieving using 0.1294 nm X-rays. Note that an X-ray pattern had been recorded earlier using BigDiff at the Photon Factory, Japan.

The pattern recorded at room temperature at 0.08 nm (Figure 1) closely resembled that from tetragonal Zr_2Ni , but with the high resolution of the X7A peak splitting indicative of a triclinic distortion could be seen. A reasonable fit could be obtained assuming a body-centered cell with $a=0.6802$, $b=0.6812$, $c=0.5691$ nm, $\alpha=90.22^\circ$, $\beta=89.83^\circ$, $\gamma=89.68^\circ$. There was some evidence of even more peak splitting, and the presence of additional peaks not indexed on the above cell was confirmed by the measurements made at longer wavelengths.

Further measurements were made with a capillary sample, using wavelength 0.08 nm, at temperatures above room temperature. At 106°C , the highest temperature measured, the main phase was clearly tetragonal (Figure 1), with $a=0.6816$, $c=0.5675$ nm. Additional weak peaks, not indexed on the tetragonal cell, were attributed to a second phase present in small amounts. On cooling (below about 95°C), the main phase transforms to a lower symmetry (triclinic) structure and the minor phase persists. The minor phase is thought to be responsible for the unaccounted peaks seen at high resolution at room temperature. We are presently examining the higher temperature patterns in an attempt to identify the second phase present in our sample. If successful in this, we are confident a two-phase analysis of the X-ray and neutron data will lead to a complete structure solution.

Figure 1. Diffraction patterns from Zr_2NiD_5 recorded at 0.08 nm using X7A. The upper pattern was recorded at 106°C and the lower at room temperature.

Michael C. Martin, D.E. Cox, and G. Shirane (BNL Physics), Y. Endoh and K. Hirota (Tohoku University), Y. Moritomo and Y. Tokura (University of Tokyo and Joint Research Center for Atom Technology)

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is in the family of the recently discovered giant magnetoresistance (GMR) materials which is caused by an as yet unknown mechanism. It is a metallic ferromagnet with a Curie temperature of $\sim 380\text{K}$. The structure of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is known to be rhombohedral with an R_{25} phonon mode condensation resulting in an $R\bar{3}c$ point group [3]. We accurately measured the a and c hexagonal unit cell lattice constants as a function of temperature, as shown in Figure 1. As the sample is cooled through the Curie temperature, a decreases more rapidly causing a decrease in the unit cell volume.

Full Rietveld analysis was carried out on powder diffraction scans at sample temperatures of 433K (above T_c), 298K, and 14K. We did not find evidence for any static Jahn-Teller type distortions above or below T_c . Nor did the Debye-Waller factor for the oxygen atoms agree with a recent polaron theory [4] which expected it to decrease below T_c .

We conclude that the structure of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is $R\bar{3}c$ at all temperatures and that polaronic effects above T_c are small if any. Further studies will include different stoichiometries to explore the relations between structure and GMR phenomena.

[3] Michael C. Martin et al., Phys. Rev. B *to be published*.

[4] A.J. Millis et al., Phys. Rev. Lett. 74, 5144 (1995).

Figure 1. $R\bar{3}c$ lattice parameters as a function of temperature. The hexagonal unit cell is used; solid lines are fits to quadratic temperature dependencies and the error bars are shown smaller than the data point symbols.

Ab-initio structure solution from powder data using resonant scattering *

X7A

R. J. Papoular, D. E. Cox (BNL), and W. Prandl (U. Tubingen)

In a recent paper, a method was proposed for the ab-initio solution of unknown structures based on the derivation of partial Patterson maps of resonant scattering atoms from synchrotron x-ray powder data obtained at three different wavelengths, two close to the absorption edge and one off-edge [1]. We have applied this method for the first time to high-resolution powder data collected from a reference material, SrSO_4 , at energies about 13, 256 and 5132 eV below the Sr K-edge. The sample consisted of a weighed mixture of SrSO_4 and diamond dust loaded into a glass capillary, the diamond serving as an internal standard to allow scaling of the three data sets on an absolute basis in the subsequent analysis.

A key feature of the work was the use of Maximum Entropy methods to allow for reconstruction of a Patterson map from both non-overlapped and overlapped peaks which is as noiseless and as free of truncation effects as possible, as shown in Fig.1. In this simple case, the coordinates of the Sr atoms can be obtained directly from the entropic Patterson sections. Not only does this procedure yield the Patterson Fourier coefficients, but also the cross-terms between the normal structure factor and the purely Sr part, from which it is possible to derive the phases of the non-overlapped reflections in the off-edge data set. Maximum Entropy methods were then used to reconstruct the total electron density of SrSO_4 , following which structure refinement was completed with standard Rietveld techniques.

[1] W. Prandl, *Acta Cryst. A* 50, 52 (1994).

Figure 1. Partial Patterson maps of Sr alone for sections at $z = 0.0, 0.19$ and 0.50 respectively, from which Sr coordinates $0.16, 0.25, 0.19$ are deduced.

The Symmetry of Garnets on the pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) - enstatite (MgSiO_3) join. *

X7A

J. B. Parise, Y. Wang (SUNY, Stony Brook), G. Gwanmesia (Delaware State, Dover), J. Zhang, R. C. Liebermann and D. J. Weidner (SUNY, Stony Brook)

Garnet phases rich in the majorite component, the high pressure polymorph of enstatite (MgSiO_3) are considered important constituents of the earth's upper mantle above the 670-km velocity discontinuity. While most garnets along the important compositional series from enstatite to pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) are thought to be cubic, the (MgSiO_3)-rich members of this series are considered to be tetragonal. The end-member composition, MgSiO_3 , has been studied by x-ray scattering methods and determined to be tetragonal [1,2]. We have begun an investigation of the join with the intention of determining the symmetry, equations of state and acoustic properties of the materials in this series.

Four compositions along the $\text{Mg}_4\text{Si}_4\text{O}_{12}$ (Mj) - $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (Py) join were synthesized at 50%, 57%, 75% and 80%Mj. These preparations were carried out at approximately 17 GPa and 2000 K in the 2000-ton uniaxial split-sphere apparatus (USSA-2000) at the Stony Brook High Pressure Laboratory. Because the distortion from cubic is expected to be subtle ($c/a \leq 0.996$) powder diffraction data were collected in high resolution mode at a wavelength of $1.2081(1) \text{ \AA}$ using a Ge(111)/Ge(220) monochromator/analyzer combination.

Profile-fitting of peaks in the region of the cubic 400 reflection clearly shows the Mj80 sample possesses tetragonal symmetry and that the samples Mj50, Mj57 are cubic. The 400-reflection of the Mj75-sample on the other hand is broadened by some 50% with respect to the other samples.

Rietveld refinements were carried out with data sets collected on samples of Mj75 and Mj80 using a position sensitive detector. A model consistent with the $I4_1/a$ symmetry previously obtained for Mj100 [2] was refined successfully for the Mj80 sample, while a model with cubic ($Ia3d$) symmetry was refined using the data from Mj75. However, close inspection of the of the Mj75-pattern revealed two very weak reflections, less than 1% of the strongest intensity, consistent in position to those expected for the tetragonal symmetry. Based on these data the change from cubic to tetragonal symmetry has been tentatively placed at the composition just below Mj75.

[1] Kato and Kumazawa (1985)

[2] Angel et al. (1989) *Am. Mineral.* 74, 509-512.

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Structural studies of the metal-insulator compounds BaVS₃ and La_{1-x}Ca_xMnO₃

X7A

P.G. Radaelli (ILL), M. Marezio (CNRS-Grenoble, AT&T) and D.E. Cox (BNL)

BaVS₃ has long been regarded as one of the most interesting one-dimensional compounds displaying a temperature-driven metal-insulator (M-I) transition (~80K) as well as a hexagonal-orthorhombic structural phase transition ~240K). Recently, considerable attention has been devoted to another M-I compound, the perovskite manganese oxide La_{1-x}Ca_xMnO₃. In this system, for 0.2 ≤ x ≤ 0.4, the M-I transition is coupled with ferromagnetic spin ordering, and T_{M-I} coincides with the Curie temperature T_C. Both temperatures are raised in an applied magnetic field, thereby producing a giant magnetoresistive (GMR) effect. For x ≈ 0.5, with decreasing temperature, the compound becomes first ferromagnetic (~225K), then antiferromagnetic (~155K), due to competition between double exchange and superexchange magnetic coupling. Temperature-dependent data were obtained at the X7A beamline on well-characterized powder samples of BaVS₃ and La_{1-x}Ca_xMnO₃ (x = 0.25, 0.50 and 0.67), using a wavelength of 0.7015 Å and a Ge(220) analyzer crystal in the diffracted beam. The structural and M-I transitions of BaVS₃ are evident in the behavior of the lattice parameters and of the unit cell volume (Figure 1). In particular, the data confirm the second-order nature of the structural transition, and indicate that, at the M-T transition, there is a sudden volume increase with decreasing temperature, consistent with recently obtained dilatometric results[1]. For La_{1-x}Ca_xMnO₃, the magnetic and M-T transitions are associated with significant lattice changes. For x = 0.25, there is a significant volume contraction at T_C (ΔV/V ≈ 0.0013, Figure 2). This effect is much too large to be due simply to magnetostriction, and it is likely to be due to the increase of the metallic nature of the bonds[2]. The x = 0.50 sample shows much larger changes of the lattice parameters at the magnetic transition[2]. Through a relatively broad region with an onset at ~220K, the b lattice parameter drastically decreases, while those along the a- and c-axes increase. Rietveld refinements based on X7A extended data sets, later confirmed by neutron powder diffraction data, indicate that these anomalies are associated with a Jahn-Teller-type distortion of the MnO₆ octahedra.

[1] T. Graf, D. Mandrus, J.M. Lawrence, J.D. Thompson, P.C. Canfield, S.-W. Cheong and L.W. Rupp, Unpublished (1994).

[2] P.G. Radaelli, D.E. Cox, M. Marezio, S.-W. Cheong, P.E. Schiffer and A.P. Ramirez, to be published in Phys.Rev.Lett(1995).

Figure 1. Lattice parameters and unit cell volume of BaVS₃ as a function of temperature.

Figure 2. Lattice parameters and unit cell volume of La_{0.75}Ca_{0.25}MnO₃ as a function of temperature.

Polymer Fiber Morphology Assessment Using Real Space Analysis of X-Ray Diffraction Data

X7A

H. D. Rosenfeld and R. Barton, Jr. (DuPont)

We have developed a method of assessing polymer fiber morphology using real space analysis of synchrotron x-ray diffraction data. This method yields percent crystallinity, crystallite size, and a histogram describing the probability of finding a crystallite with its c-axis tilted theta degrees from the fiber axis. It is applicable to both well-crystallized and poorly crystalline samples, and is independent of assumptions regarding the so called disordered polymer phase. The method requires two diffraction scans per sample (equatorial and meridional), the ability to access the momentum transfer range 0.5 Å⁻¹ ≤ q ≤ 18 Å⁻¹, low background, and high intensity. Since X7a provides the required beamline characteristics, it was used to test the method on several samples of NOMEX* aramid. Our results demonstrated the ability of real space analysis of polymer fiber morphology, using synchrotron x-ray diffraction data, to accurately describe NOMEX* samples with widely different degrees of crystallinity and orientation. The method has since been tested successfully on Nylon fibers using data collected at the X3a1 and X20b beamlines.

It is our expectation that it is applicable to a wide range of polymer fiber systems.

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Study of atomic structure in PMN single crystal using resonant x-ray diffraction *

X7A

S. Teslic and T. Egami (U. of PA), S. Vakhrushev (Ioffe Inst., St. Petersburg, Russia)

We have studied the atomic structure of a PMN ($\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$) single crystal using resonant x-ray scattering near the Pb L_{III} and Nb K_α absorption edges. Superlattice peaks $1/2<1,1,1>$ have been observed in PMN by electron diffraction and were used in support of a two-phase Nb/Mg ordering model to explain the relaxor ferroelectric behavior of PMN. However, the microscopic origin of the superlattice peaks has been controversial. Our results shown below indicate that Nb is heavily contributing to this peak, which is consistent with the idea of Nb/Mg, or Nb/ $(\text{Mg}_{2/3}\text{Nb}_{1/3})$, chemical ordering. However, the effective scattering factor of this peak is about 6, while for full ordering should be close to $DZ = 29$. This discrepancy cannot be explained by oxygen participation, since oxygen tends to move toward Nb^{5+} which is smaller and higher in valence, thus exacerbate the discrepancy. On the other hand, the Pb atoms are displaced toward Mg atoms since Pb-Mg repulsion is weaker than the Pb-Nb repulsion. This Pb displacement will compensate the difference in the scattering power between Nb and Mg and make the effective smaller. Then Pb must be polarized in antiferroelectric manner, while the sample has random local ferroelectric polarization resulting in the relaxor ferroelectricity. Indeed the data at the Pb edge show a negative contribution to the structure factor from Pb but it is too small. We believe that dominant factor must include both chemical ordering (possibly forming of Nb and Mg clusters) and correlated atomic displacements.

Figure 1. Intensity of the $(1/2, 1/2, 5/2)$ peak as a function of energy near the Nb K-edge.

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Figure 2. Intensity of the $(1/2, 1/2, 5/2)$ peak as a function of energy near the Pb L-edge.

Pair Distribution Function (PDF) Studies of the Impact of Processing Chemistry on Local Order in PZT Solid Solutions *

X7A

A. P. Wilkinson (Georgia Tech), S. Teslic, T. Egami (U. Penn.), Q. Zhu, and D.E. Cox (BNL)

An inhomogeneous distribution of cations on the B sublattice of perovskite ferroelectric solid solutions is known to have important consequences for the materials dielectric properties. In many materials it leads to relaxor behavior and properties that are desirable in devices such as mechanical actuators. The distribution of cations in perovskite solid solutions is known in some cases to be dependent on the processing conditions used, for example, in lead scandium tantalate.

We are exploring the impact of sol-gel processing chemistry on solid solution homogeneity and the dielectric properties of a series of ferroelectrics including PZT ($\text{Pb}[\text{Zr}_{1-x}\text{Ti}_x]\text{O}_3$). Initially, two samples of PZT 33/67 prepared using slightly different processing conditions were examined. Data were collected for both samples using a wavelength of $0.4986 \text{ \AA}$ over the range $Q = 0.6 - 24.3 \text{ \AA}^{-1}$. Pair distribution functions were calculated for each of the samples using Rosenfeld's X-ray PDF package. The PDFs indicate that the different processing conditions used in the preparation of the two samples led to different local structure in the solid solutions.

Further data analysis and complementary neutron studies are currently underway.

* We are grateful to Georgia Institute of Technology for the financial support of this work.

Structural and electronic properties of GaN films grown on sapphire by molecular beam epitaxy *

X7A

Q. Zhu (BNL), A. Botchkarev, W. Kim, O. Aktas, A. Salvador, B. Sverdlov, H. Morkoç (U. of Ill., Urbana-Champaign), S. -C. Y. Tsen, and D. J. Smith (Arizona State U.)

GaN and related materials, thanks to the recent breakthrough [1], have demonstrated tremendous potential for applications in short wavelength optoelectronics and high temperature/power electronics [2]. Despite the technological importance of GaN, correlation between microstructure and the physical properties is still lacking.

The structural characteristics of GaN films grown on sapphire substrates by molecular beam epitaxy (MBE) have been investigated using high-resolution synchrotron x-ray diffraction and electron microscopy, and compared to their electrical and optical properties. We find remarkable correspondence between the in-plane structural order (coherence length and mosaic spread) and the electrical and optical properties. Contrary to common belief, our observations show unequivocally that the out-of-plane structural features, which are considerably better developed than the in-plane counterparts, can not be used for determining the material quality with respect to their optical and electrical activity. In particular, the (00l) mosaic spread is not a good indicator of film quality [3]. The structural correlations of the GaN film, the AlN buffer layer and the sapphire substrate are explored and compared to their growth conditions. The issue of in-plane stacking fault (hcp - fcc) is also addressed using x-ray scans along the (10l) direction. We find no significant feature of stacking disorder due to fcc-to-hcp defects in all these films, which is consistent with the TEM observation.

- [1] H. Amano *et. al.*, Jap J. Appl. Phys. **28**, L2112, (1989).
- [2] H. Morkoç, *et. al.*, Science **267**, 51 (1995).
- [3] Q. Zhu *et. al.* Appl. Phys. Lett. (submitted).

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Polymer and dimer formation in alkali-metal intercalated C₆₀ *

X7A

Q. Zhu, D. E. Cox, (BNL) and J. E. Fischer (U. of Penn.)

Rocksalt-type MC₆₀ has been a subject of tremendous interest since its early discovery [1]. Its high-T structure is similar to the superconducting M₃C₆₀ compounds, but with only one charge transfer. Band structure calculations predicted rocksalt MC₆₀ to be a metal, however all the experiments indicated otherwise. Separately, Na₂MC₆₀ exhibits anomalously low T_c which deviates from the T_c vs. lattice constant relation according to BCS theory.

Synchrotron x-ray powder diffractions revealed common tendency for C₆₀ ions in both materials to coalesce and to form dimers [2] and polymers [3,4]. Our results [2] indicated that in competition with polymer formation and with equilibrium phase separation (α -C₆₀ ($0 < x < 0.1$) plus K₃C₆₀), the cubic *monoanionic* KC₆₀ transforms to a metastable orthorhombic *dimer* phase with a 9.34 Å center-to-center separation. It is obtained by quenching from above 423 K to 298 K and *immediately* cooling below 270 K. On the other hand, the cubic *trianionic* fulleride superconductors Na₂RbC₆₀ and Na₂CsC₆₀ exhibit a reversible conversion into orthorhombic polymers under modest pressures (≤ 3 kbar) and ambient temperature [4]. Structure refinement based on high-resolution synchrotron powder x-ray profiles reveals polymer chains with 9.35 Å intermolecular separation, comparable to that in the metastable *monoanionic* dimer and polymer phases of KC₆₀ and RbC₆₀ [2,3]. These examples reinforce current ideas about the necessary conditions for fullerene/fulleride intermolecular bonding, namely reduced inter-C₆₀ spacing and an adequate degree of molecular rotational dynamics.

- [1] Q. Zhu *et. al.*, Phys. Rev. B **47**, 13948 (1993).
- [2] Q. Zhu, D. E. Cox, and J. E. Fischer, Phys. Rev. B **51**, 3966 (1995).
- [3] P. W. Stephens *et. al.*, Nature **370**, 636 (1994).
- [4] Q. Zhu, Phys. Rev. B **52**, R723 (1995).

Figure 1.

Figure 2.

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Calcareous sponge spicules: presence of amorphous and crystalline phases in the same element *

X7B

J. Aizenberg, L. Addadi, S. Weiner (Weizmann Institute of Science, Israel), J. Hanson, T.F. Koetzle (BNL)

Some organisms form stable minerals that would never precipitate under ambient conditions in an inorganic environment, or if formed are unstable precursors of more stable compounds. One of the most fascinating examples is biogenic amorphous calcium carbonate, because its transformation into crystalline polymorphs is not only thermodynamically favored, but also kinetically fast. The calcareous sponges (Porifera) form a wide variety of spicules, each of which is generally thought to be composed of a single crystal of Mg-bearing calcite. Differences have, however, been observed between the spicule mineral and inorganically formed calcite crystals.

Our attention was drawn to the fact that an additional amorphous mineral phase may be present, by the observation that the intensities of the diffracted beam from single *Clathrina* triradiate spicules (100 microns across) accounted for only about 20% of the expected value of an equivalent volume of a pure single calcite crystal. To investigate this phenomenon, synchrotron powder diffraction data were collected for *Clathrina* spicules and compared to analogous measurements of two controls: (i) pure calcite and (ii) spicules of the ascidian *Pyurapachydermatina* which are composed entirely of amorphous CaCO_3 . The samples were finely ground, and 0.3 mm glass capillaries were filled completely with the powder to ensure that the same amount of material was subjected to the X-ray beam in each experiment. Narrow slit measurements were performed with a step size of 0.01 deg and sampling time of 10 sec/step using the Huber diffractometer.

The powder X-ray diffraction pattern (below) of *Clathrina* spicules shows in addition to the sharp calcite reflections, an intense but broad peak around $2\theta = 15$ deg, indicative of the presence of an amorphous phase.

On the basis of these and addition electron microscope observations, we deduce that the spicule is composed of a core of calcite embedded in a thick amorphous calcium carbonate layer and apparently covered by a thin calcitic sheath. The formation of composite structures in which amorphous and crystalline phases coexist apparently endows the biogenic material with advantageous properties, that may be interesting to investigate.

Figure 1.

* US DOE contract DE-AC02-76CH00016 Div of Chem. Sci. Office of Basic Energy Science and US-Israel Binational Sci. Foundation

Biologically-induced reduction in symmetry at the level of the crystal domain shape

X7B

J. Aizenberg, L. Leiserowitz, S. Weiner, L. Addadi (Weizmann Institute of Science, Israel), J. Hanson, and T.F. Koetzle (BNL)

Organisms can exert a remarkable degree of control over crystal growth. One means of achieving this is by the adsorption of specialized macromolecules on specific planes of the growing crystals. With continued growth of the crystal, the macromolecules are incorporated inside the crystal bulk. In previous studies we observed that this strategy used to control single crystal texture and morphology, may result in an effective reduction in crystal symmetry at the level of the microscopic domain shape. In this study we have examined in detail one type of calcareous sponge spicule, that is a beautiful example of how the biological environment induces a reduction in crystal symmetry. The *Sycon* asymmetric triradiate spicule was specifically chosen for this study, because each is composed of a single crystal of calcite, but their morphologies do not reflect the hexagonal symmetry of calcite. Two rays of each spicule develop perpendicular to the symmetry-related (-102) and (1-12) planes, and the third ray grows perpendicular to the (0-16) calcite plane.

The diffraction peak profiles in the ω - and $\omega/2\theta$ -scan modes were monitored for control synthetic calcite crystals and four triradiate spicules. Two spicules were measured intact, two others were subdivided into three different rays and each was studied separately. Fig. 1 shows diffraction peak profiles of the representative {104} and {012} families of reflections for three rays of the same spicule. In every case reduction in symmetry is observed in the coherence lengths among symmetry-related crystallographic directions. Larger coherence lengths and smaller angular spreads are observed in the crystallographic directions coincident with, or close to, the directions of the morphological axes of the spicule rays. The reconstructed shapes of the domains of perfect structure unequivocally show the extent of reduction in symmetry that can be achieved for each of the growing subunits of the same crystal (Fig. 2). The average shapes of highly anisotropic perfect domains of each spicule ray reflect to a remarkable degree the macroscopic morphology. The synthetic crystals show no such reduction in symmetry.

Although the manner by which such exquisite control is achieved is not known, we envisage it involving a combination of oriented nucleation with either physical or stereochemically-driven adsorption. Support: US DOE contract DE-AC02-76CH00016 Div of Chem Sci., BES and US-Israel BSF

Figure 1.

Figure 2.

Thermal decomposition of silvercarbonate studied by powder diffraction methods. *

X7B

E. Krogh Andersen, I.G. Krogh Andersen (U. Odense, DK), P. Norby, J.C. Hanson (B NL)

Silvercarbonate is a thermally unstable compound, which when heated will decompose into silveroxide and carbondioxide. By further heating silver oxide is decomposed into a fine powder of pure silver and oxygen. The transformations are clearly visible as silvercarbonate is a greenish powder, silver oxide is pitch black and the silver metal is obtained as a white/yellowish powder. We intend to study the structural detailed involved in the thermal decomposition process, and as a preliminary experiment powder diffraction data were collected using a Translating Image Plate System. Figure 1 shows the powder diffraction profiles extracted from the image plate data as a function of temperature. The transformations are clearly visible as distinct changes in the diffraction patterns. Figure 2 is a small section of the image on the Image Plate, showing the same section as in Figure 1. A closer examination of the diffraction patterns reveals that immediately before the phase transformations changes in the powder diffraction patterns occurs indicating changes in the crystal structure. Powder diffraction data obtained from image plates are suitable for Rietveld refinement and the structural changes preceding the decomposition reactions will be further investigated.

Figure 1. Powder diffraction patterns showing the decomposition of silver carbonate.

* This work was supported under contract DE-AC02-76CH00016 with the US Department of Energy by its Division of Chemical Sciences, Office of Basic Energy Sciences and by the Danish Natural Science Research Council

Figure 2. TIPS image of the decomposition of silver carbonate.

A Synchrotron X-Ray Study of Piezoelectric Moduli, Ferroelectric Switching and Domain Reversal in CsTiOAsO₄ and KTiOPO₄ under an Applied Electric Field *

X7B

Rindert Bolt, Joergen Albertsson and Goeran Svensson, Inor. Chem., CTH, Gothenburg, Sweden, Kenny Stahl, Inor. Chem. 2, Lund Univ., Lund, Sweden, and J. C. Hanson, BNL

Single crystals of isostructural cesium titanyl arsenate (CTA) and Sc³⁺ doped potassium titanyl arsenate (KTP) with space group Pna2₁ have been grown by the top-seeded solution growth technique from self-fluxes. Extended face plates were cut and polished to a thickness between 300 and 450 μm along [001]. A layer of approximately 200 Å of Au (CTA) or Al (KTP) was evaporated on the {001} faces leaving a window frame without electrode material on the edge of the faces. Electric leads were connected to the metal layers. X-ray data (λ = 0.89198 Å) were collected at beamline X7B at NSLS using a Huber six-circle diffractometer with Na(Tl)I scintillation detector and monitor. The electric field experiments were made in a setup similar to the one used by Stahl, Kvik & Abrahams [Acta Crystallogr. (1989). A46, 478-475]. Each electric lead on the crystal plate was connected to a power supply and a generator producing a 20 Hz square wave variable voltage of up to 1500 V and with the tension alternatingly applied to each side of the crystal. A scaler and a clock were gated to each of the two square-waves, thus allowing a detection of the shift in omega and intensity between the two field directions. The data from CTA were collected at room temperature and those from KTP at 150 K with a Displex close-cycle refrigerator.

The splitting of the Bragg peaks (δω) as a function of the electric field strength provide information about the piezoelectric strain tensor, coercive field and domain reversal mechanisms of the investigated materials. The strain produced in the z direction by the electric field is given by ε₃ = d₃₃E₃ which combined with Bragg's law results in d₃₃ = -δ(θ)/(2E₃tan(θ)). Values d₃₃ = 33 and d₃₁ = 2 pm/V were estimated for CTA from the peak splits of 00l and h00 reflections at 1330 V/mm.

For CTA and KTP the peak splits increase with the field strength to maxima at about 2000 (CTA) and 3300 V/mm (KTP) after which the values decrease to about 1/10 at 2600 (CTA) and 3500 V/mm (KTP). Above the latter field strengths a single domain is switched 40 times per second by the alternating field, i.e. these values may be taken as estimates of the coercive fields.

If the strong field is applied in only one of the two directions, estimates can be made of the field strength necessary to switch the domain just once. These values are dependent on the polar direction of the crystal outside the metal covered area. If the final directions are the same, the domain walls can move inward from the outer edge and a low field is sufficient for the reversal. If the final directions are opposite, a domain nucleation mechanism is required for the metal covered part of the crystal so a high field must be applied to reverse the polarity. Using the 0 0 16 reflection of CTA, field strengths of 560 and 1550 V/mm were determined for the two cases.

* Work supported under contract AC02-76CH00016 with US DOE by its Div of Chem. Sciences, Office of Basic Energy Sciences, the Swedish Natural Science Council and European Commission

Development of Synchrotron Diffraction Methods for Structure Determination with Small Single Crystals *

X7B

R. W. Broach, UOP Res.; J. J. Pluth, Univ of Chicago; R. M. Kirchner, Manhattan College; J. C. Hanson, BNL; J. Phillips and J. Falt, Siemens Anal. Inst.

Although a single crystal study is the simplest, quickest, and most complete way to determine the crystal and molecular structure of a molecular sieve, it is sometimes not possible because large enough crystals can not be synthesized. We have begun exploratory studies to develop methods and experience with structure determination from small crystals.

The structure of the mineral Raite, $\text{Na}_4\text{Mn}_3\text{Si}_8(\text{O},\text{OH})_{24}\cdot 9\text{H}_2\text{O}$, is not known. Data were collected for a small crystal of dimensions $5\times 5\times 110$ cubic microns using the Siemens CCD detector. A total of 5545 diffractions were collected, of which 1833 were greater than 1 sigma, 832 greater than 2 sigma, 301 greater than 3 sigma and 96 greater than 4 sigma. We are currently trying to solve the structure using this weak data set.

Data were collected for a $30\times 30\times 30$ cubic microns crystal of the zeolite Sodalite, $\text{Si}_{12}\text{O}_{24}\cdot 2\text{C}_2\text{H}_4(\text{OH})_2$. Refinement of the crystal structure using the CCD data gave results in good agreement with previously published data. The final R value of the refinement was 0.041 compared with 0.024 for data collected using a Cu target rotating anode generator.

Another data set was collected for the mineral Diopside, $\text{CaMg}(\text{SiO}_3)_2$. This sample is being used to test the quality of the CCD data.

Refinement of the structure is in progress.

The structure of the titanosilicate mineral zorite was reported by Sandomirskii and Belov. Difficulties in measuring the intensities of the diffuse reflections made it possible to solve only the superposition structure using the point reflections and a unit cell with half the true c-axis length. We have synthesized small crystals of synthetic analogues to zorite, which may not have the same disorder. So far, we have been able to see a few diffraction spots using the image plate detector, but not with the CCD system. A higher brilliance beam line is probably needed.

We have recently synthesized a new class of zinc phosphate-based molecular sieves. Some of these phosphate-based sieves have zeolite analogues, such as SOD, FAU, and RHO; and some have new structures. We have one material which appears to be orthorhombic with very similar a, b, and c axis lengths. The similarity of the axis lengths causes severe overlap in the powder diffraction pattern, even when using high resolution synchrotron data, and makes it difficult to accurately extract peak intensities for structure solution. Individual crystals appear well-shaped but of maximum size about $3\times 3\times 12$ cubic microns in size. No diffraction spots were seen using the image plate or CCD. A higher brilliance beam line is probably needed.

* This work was supported by contract DE-AC02-76Ch000016 with the US DOE by Div of Chemical Sciences, Office of Basic Energy Sciences

In-situ powder diffraction studies of zeolite syntheses; Magnesium substituted aluminophosphates. *

X7B

A. Nørlund Christensen (U. Århus), Poul Norby (BNL)

In-situ powder diffraction was used to follow the syntheses of magnesium substituted aluminophosphate molecular sieves. Substitution of trivalent aluminum into the tetrahedral framework of aluminophosphates with divalent cations is important in order to tailor catalytical properties of the materials.

Magnesium substituted aluminum phosphates (MAPO's) were synthesized from pastes made from the following chemicals: MgO or $\text{Mg}(\text{Ac})_2\cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{OH})_3\cdot \text{H}_2\text{O}$ (Catapal), 85 % H_3PO_4 , NaOH , 37 % HCl , and the templates triethylamine (Et_3N), tripropylamine (Pr_3N), di-n-propylamine (Pr_2NH), and tetramethylammonium hydroxide (Me_4N^+). Molar ratios of pastes:

A: $1.5\text{Et}_3\text{N}$, $0.02\text{Na}_2\text{O}$, 0.2MgO , Al_2O_3 , P_2O_5 , $27.8\text{H}_2\text{O}$ B: $1.5\text{Pr}_2\text{NH}$, 0.2MgO , Al_2O_3 , P_2O_5 , $25.0\text{H}_2\text{O}$ C: $2.0\text{Pr}_2\text{NH}$, 0.3MgO , $0.85\text{Al}_2\text{O}_3$, P_2O_5 , $25.0\text{H}_2\text{O}$ D: $1.91\text{Pr}_3\text{N}$, 0.17MgO , $0.96\text{Al}_2\text{O}_3$, P_2O_5 , $25.2\text{H}_2\text{O}$ E: $2.19\text{Me}_4\text{N}^+$, 0.21HCl , 0.29MgO , $0.81\text{Al}_2\text{O}_3$, P_2O_5 , $32.0\text{H}_2\text{O}$ The in situ measurements of the crystallization of the amorphous gels at temperatures up to 200°C showed in most cases the appearance of precursor phases formed before the formation of the final products.

Some of the precursor phases have not yet been identified.

The obtained results are the following:

A: Precursor is $\text{MgAl}(\text{PO}_3\text{OH})_2\text{OH}\cdot 6\text{H}_2\text{O}$. Products are MAPO-47 and MAPO-5. The growth rate of MAPO-5 is faster than that of MAPO-47. At 130°C MAPO-5 is only formed in minor quantities and MAPO-47 is the main reaction product. At 180°C MAPO-5 and MAPO-47 are formed in approximately equal amounts.

B: Two unidentified precursor phases are formed. At 120°C a sodalite like phase is formed. At 200°C the reaction product is a mixture of MAPO-46 and MAPO-39.

C: Two unidentified precursor phases are formed. At 200°C the reaction product is a mixture of MAPO-39 and MAPO-46. The formation of MAPO-46 is faster than that of MAPO-39.

D: The reaction product in the temperature range $25 - 200^\circ\text{C}$ is MAPO-36 E: At temperatures up to 75°C the precursor phase $\text{MgAl}(\text{PO}_3\text{OH})_2\text{OH}\cdot 6\text{H}_2\text{O}$ is formed. At temperatures from 90 to 120°C a sodalite like phase is formed.

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Time Resolved Dehydration Studies of the Layered Aluminophosphate $d,l\text{-Co(en)}_3 \text{Al}_3\text{P}_4\text{O}_{16} \cdot x\text{H}_2\text{O}$ *

X7B

M. J. Gray, A. P. Wilkinson (Georgia Tech), P. Norby and J. Hanson (BNL)

The increasing level of interest in optically pure organic compounds, particularly in the pharmaceutical industry, has provided impetus for the design and synthesis of potential chiral sorbents and catalysts. We have synthesized a number of aluminophosphate and gallophosphate materials using chiral transition metal coordination complexes as templates.^{1,2}

The layered material, $d,l\text{-Co(en)}_3 \text{Al}_3\text{P}_4\text{O}_{16} \cdot x\text{H}_2\text{O}$, was studied using time resolved x-ray diffraction. Samples contained in capillary tubes were dehydrated under flowing dry nitrogen while diffraction data were obtained using a scanning imaging plate detection system. Data were collected as a function of time at various temperatures and while the temperature was ramped. Several interesting phenomena were observed, the most significant of which was the transformation to another phase with a markedly smaller interlayer spacing during dehydration.

Further data analysis is now underway to determine the structure of the dehydrated end product and examine the kinetics of dehydration.

1. D. A. Bruce, A. P. Wilkinson, M. G. White, and J. A. Bertrand, *J. Chem. Soc. Chem. Commun.*, 2059-2060, 1995.

2. D. A. Bruce, A. P. Wilkinson, J. A. Bertrand, M. G. White and J. C. Edwards, submitted for publication.

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Synthesis of zeolite A from thermally activated natural kaolinites. *

X7B

Alex F. Gualtieri (Univ. of Modena, Italy), P. Norby and J. Hanson (BNL), and G. Artioli (Univ. of Milan, Italy),

Zeolite A is by far the most studied zeolite and the most employed zeolitic material for industrial purposes [1]. It can be synthesized using clay minerals such as kaolinite [2]. In order to activate the kaolinite for the reaction, it is necessary to perform a thermal treatment at about 600-800 °C [3]. The experiments we performed deal with the formation of zeolite A from two kaolinites with a different density of structural disorder. The samples are Kga-1 and Kga-2, international standards from Georgia, USA exhibiting a different density of planar faults [4]. The samples are activated at 800 °C. The syntheses are achieved by hydrothermal leaching of the activated powders throughout a NaOH solution in the temperature range 70-110 °C. The solution is cleansed by means of a 0.5 mm diameter syringe in a 0.7 mm Lindemann glass capillary. The applied pressure inside the capillary is 10 Atm. The reaction syntheses are followed by angular dispersive experiments. The detector used is a translating Imaging Plate. The isothermal experiments are performed at 70, 80, 90, 100, 110 °C. The heating rate used to reach the set temperature is about 100 °C/min. The reaction is followed by observing the modification of the intensity of the scanned portion of the diffraction rings as a function of time. The image collected and stored in the plate is scanned using a He-Ne laser beam stimulation in an IP Fuji BAS2000 scanner. The integrated intensities are normalized and transformed into phase fractions and conversion values to plot the α /time curves. The conversion vs. time plots enable to elaborate on the kinetic mechanism of the reaction process and to calculate the value of the activation energies and frequency factors. n in both cases is greater than 4 thus the process can be described as an interface controlled acceleratory reaction with random nucleation (increasing rate) and 3D growth (constant rate) of the crystals of the cubic phase. When the coefficient n of the Avrami equation is so large the rate limiting step of the reaction may be the coalescence and impingement of the forming nuclei. n has a tendency to drop at higher temperature and this can be directly related to the decrease of the random nucleation rate for thermodynamic reasons. In fact, at higher temperature, hydroxysodalite phase is more stable than (Ostwald's law) and the decrease of the nucleation rate for both samples is due to a competition of forming nuclei of the two phases.

[1] Drag E.B., Miecznikowski A., Abo-Lemon F. and Rutkowski M. (1985). Synthesis of A, Xe Elsevier Science Publishers.

[2] Kerr G.T. (1966). *J. Phys. Chem.* 4, 1047-1050.

[3] Barrer R.M., Cole J.F., Sticher H. (1968). *J. Chem. Soc. (A)* 10, 2475-2485.

[4] Gualtieri A.F. (1966). PHD thesis. Univ. of Modena (Italy).

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Rietveld refinement of synchrotron data collected in transmission geometry using an Imaging Plate detector: application to standard $m\text{-ZrO}_2$ *	X7B
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Alex F. Gualtieri (Univ. of Modena, Italy), P. Norby, J. Hanson and J. Hriljac (BNL), and G. Artioli (Univ. of Milan, Italy)

We have performed the Rietveld refinement of $m\text{-ZrO}_2$ (standard material selected by the commission on powder diffraction of the IUCr to undertake a round robin of Rietveld refinement). The data were collected at X7B using a flat Imaging Plate detector, which is a powerful tool when fast data collections are required. An example is real-time studies where a sample is analysed "in situ" at H/LT, H/LP, under constant gas stream, etc. The IP is composed of a metal slide supporting a 0.5 mm thick plate (20×40 cm) made of a flexible plastic material coated with fine storage phosphor crystal (BaFBr:Eu^{2+}) mixed with an organic binder [1]. The photostimulable phosphor is capable of storing a fraction of the absorbed X-ray energy. When later stimulated by visible light, it is capable of emitting photostimulated luminescence (PSL), the intensity of which is proportional to the absorbed X-ray intensity. The details of the mechanism are well described in [1] and [2].

Prior to the collection, the sample was ground, sieved and mounted on a 0.3 mm Lindemann quartz capillary and placed on a standard goniometer head. The accurate value of energy ($\lambda = 0.9583 \text{ \AA}$) is calibrated using the standard material LaB_6 . The exposure time is 10 min and the pattern is collected in the range $0-64.5 2\theta$ ($\sin\theta/\lambda = 0.55$).

The data reduction accounts for a variety of corrections embracing the polarization of the synchrotron beam, the Lorentz factor, the absorption, the correction for the flat IP geometry, and the IP zero shift. The corrections produce working data suitable for a Rietveld refinement using the programs: 1) a modified for Imaging Plate data version of The X-Ray Rietveld System XRS-82 Baerlocher (1982); 2) General Structure Analysis System GSAS (Larson & Von Dreele, 1995). The agreement factors (R_p s) are lower than the values reported in the IUCr round robin for synchrotron data because the instrumental resolution is intrinsically poorer in this geometry despite the use of a synchrotron source.

The refined unit cell constants and the atomic positions are consistent with the single crystal data. The refined thermal parameters are in close proximity to the single crystal data showing that it is possible to get reliable and consistent thermal parameters in Debye-Scherrer geometry using synchrotron radiation. We can state that an accurate data reduction of the transmission data collected using synchrotron radiation provide Rietveld refined parameters of sufficient accuracy and precision.

[1] Amemija, Y. (1990). *Synch. Rad. News* 3, 21-26.

[2] Bourgeois, D., Moy, J.P., Svensson, S.O. & Kwick, Å. (1994). *J. Appl. Cryst.* 27, 868-877.

[3] Baerlocher, C. (1982). *Inst. für Krist. & Petrogr., ETH, Zürich.*

[4] Larson, A.C. and Von Dreele, R.B. (1995). "GSAS. General Structure Analysis System," *Report LAUR 86-748*. Los Alamos National Laboratory.

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A Time-Resolved Thermal X-Ray Powder Diffraction Study on CoSAPO-34	X7B
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Microporous, microcrystalline aluminium phosphates (ALPOs), metal-substituted aluminium phosphates (MeALPOs) and silicon-substituted analogues (SAPOs) are interesting candidates for catalytic studies and there is a continuing growth in the Microporous, microcrystalline aluminium phosphates (ALPOs), metal-substituted aluminium phosphates (MeALPOs) and silicon-substituted analogues (SAPOs) are interesting candidates for catalytic studies and there is a continuing growth in the size of the family of compounds since they were first synthesised in 1982[1]. Because of their structural relationships to the zeolites the materials are often termed zeotypes. The zeotypes are monophasic crystalline solids in which the active sites are distributed in a spatially uniform manner throughout the bulk. Thus, some of them can be used as uniform heterogeneous catalysts. In this connection, the most significant feature of zeotypes is their microporous nature which means that nearly all of the accessible surface area is actually inside the crystallites. For example, over 99.5% of the surface area of a 1mm diameter crystallite is internal. Consequently, most of the Al, P and/or metal atoms are effectively surface atoms, although they are located deep inside the material. and this means that bulk physical techniques such as EXAFS can actually be regarded as surface techniques in these special cases. We have previously published some of the results of EXAFS studies using the facilities of X11A [2 - 4].

In CoSAPO-34 the cobalt atoms enters the framework by substituting Al(III) in the form of Co(II). The material is interesting because it undergoes colour changes on calcination (blue to green at 500 C with a change to greyish-blue on cooling in moist air). The object of the present study is use time-resolved powder diffraction (X7B) to map the structural changes that occur whilst the as-synthesised sample is being heated upto 500 C. The results are currently being analysed.

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[1] S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannan, E.M. Flanigen, *J. Am. Chem. Soc.* 1982, 104, 1146

[2] A. Lund, D.G. Nicholson, G. Lambie and B. Beagley, *J. Materials Chem.*, 1994, 4, 1723.

[3] M. Endregard, D.G. Nicholson, M. Stocker and G. Lambie, *J. Materials Chem.* 1995, 5, 485.

[4] M. Endregard, D.G. Nicholson, M. Stocker and G. Lambie, *J. Materials Chem.* 1995, 5, 785.

Track effects in hydrocarbon liquids exposed to x-rays *

X7B

R. A. Holroyd, J. M. Preses, J. C. Hanson (BNL - Chemistry Dept.)

Absorption of X-rays in hydrocarbon liquids leads to photoelectrons which produce dense tracks of secondary ionization. Charge recombination of these ions forms excited states in the track. The excited states will be singlet with high probability when the recombination is of geminate partners, because the spins remain correlated. As the X-ray energy decreases, the density of ionizations along the track of the photoelectron increases and the probability of recombination with ions from other ionization events will increase. This non-geminate recombination is of uncorrelated ions and the yield of singlets is expected to decrease as the X-ray energy decreases. Such "track effects" are of interest to radiation chemists and theoretical predictions¹ have been made of the magnitude of this effect.

In this study we measured the relative yield of excited singlet states for three hydrocarbons by the intensity of the UV fluorescence and as a function of X-ray energy. X-rays from 6 to 14 keV were obtained from a 311 Si crystal monochromator at X7B. The X-ray beam passed through a N₂-filled ionization chamber, to monitor the beam intensity prior to entering the sample cell. The cell was made of quartz but had a 1 mil mylar entrance window for the X-ray beam. UV fluorescence emerging from the back of the cell was collected by a spherical mirror and focused on the window of a photomultiplier tube (EMI). The fluorescence beam passed through an interference filter to cut out stray light. The tube was operated in the single photon counting mode.

The results for trans-decalin are shown in figure 1. The fluorescence yield from singlet states decreases with decreasing X-ray energy, that is, as the track density increases. The results need to be corrected for the lifetime of the excited states, τ_{obs} , which also decreases as the energy decreases; i.e.: Yield of singlets = fluorescence yield/ τ_{obs} . The results are compared with computer simulations¹, which predict a decrease in singlet yields with decreasing X-ray energy in this range (solid line). Similar results are obtained for cis-decalin and dodecane. This confirms that recombination of uncorrelated ions in the dense track leads to the formation of more triplet excited states and consequently reduces the yield of singlet excited states. Measurements will be made down to 4 keV in the near future.

[1] W. M. Bartczak, A. Hummel, Chem. Phys. Lett. 208, 232, 1993

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In-situ studies of phase transitions in silicate mesostructures *

X7B

C. C. Landry, G. D. Stucky (U.C. Santa Barbara), J. C. Hanson, and P. Norby (BNL)

Mesoporous silicates are produced by a solution templating process which involves cooperative self-assembly of the organic and inorganic regions of the material.

We have used in-situ X-ray diffraction at the NSLS to monitor phase changes in these products upon heating, with the goal of gaining control over the polymerization process. Silicate polymerization in these experiments was induced by heating the sample hydrothermally to 150 °C in quartz or glass capillaries. The detection system consisted of an image plate placed behind a slit; time resolution was accomplished by moving the image plate behind the slit at a fixed rate. After one hour of heating, conversion of the hexagonal (H_α) phase to a new rectangular phase, which we have designated R_α , was observed. This short-lived phase transformed into the cubic (Q_α) mesostructure after 8 minutes; no additional changes were observed upon cooling to room temperature.

The macroscopic structure of these inorganic/organic assemblies is dependent upon the local effective surfactant packing parameter $g=V/a_o l$, where V is the total volume of the surfactant chain plus any co-solvent molecules between the chains, a_o is the effective head group area at the micelle surface and l is the kinetic surfactant tail length. Changes in this parameter are thus directly proportional to changes in V . Small values of g tend to stabilize more locally curved surfaces (H_α) while larger values stabilize flatter surfaces (Q_α). We propose that the phase changes observed in our experiment are caused by the movement of ethanol, present in solution from hydrolysis of the inorganic precursor tetraethylorthosilicate (TEOS), into the organic micellar region at high temperatures. The changes are not reversible since the silicate becomes less flexible as it polymerizes at high temperature, fixing the Q_α phase in place. We anticipate performing further experiments aimed at gaining better control over the polymerization process through external addition of co-solvents and hydrolysis of new inorganic precursors.

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STRUCTURE	OF
A VOLATILE CALCIUM β -DIKETONATO TETRAETHYLENE-PENTAMINE CHELATE $[\text{Ca}(\text{thd})_2(\text{N}_5\text{C}_8\text{H}_{23})]$	X7B

I. Mutikainen, T. Hanninen, M. Leskela (Univ. Helsinki) and J. Hanson (BNL)

Thin films of various inorganic materials today play an important role in practical applications as well as in fundamental science: microelectronics, optics, sensors, solar cells, etc. The interest towards volatile alkaline earth and rare earth complexes has rapidly grown along the use of chemical vapor deposition (CVD) in fabrication of superconducting oxide thin films. For atomic layer epitaxy (ALE) growth of thin films sufficiently volatile compounds of copper, rare earth and alkaline earth metals must be available. So far, the best performing alkaline earth metal precursors in terms of thermal stability and volatility are the monomeric β -diketonate adducts with multidentate Lewis bases.

The crystal structure of bis(2,2,6,6-tetramethyl-heptane-3,5-dionato)calcium with tetraethylene-pentamine has been solved using synchrotron radiation at 153 K. The complex crystallizes in pentane solution as a monomeric molecule. The X-ray data of 10598 unique reflections was collected using image-plates scanned with off-line Fuji 2000 scanner. The crystals are monoclinic $P2_1/c$ (nr. 14) with $a=15.480(2)$, $b=10.874(2)$, $c=20.866(3)$ Å, $\beta=90.33(2)$ deg., $Z=4$, $R=0.085$ for 4303 reflections having $I>2\sigma(I)$.

The coordination sphere of calcium is a distorted cubic antiprism where two thd molecules coordinate to Ca via four oxygen atoms and the tetraethylenepentamine via four nitrogen atoms. One amine nitrogen is uncoordinated. The amine ligand is disordered in two positions, each conformation with site occupation factor of 0.5. The bond lengths in the Ca coordination sphere vary from 2.337(5) to 2.396(5) Å for Ca-O and 2.518(6) to 2.740(6) Å for Ca-N.

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Figure 1. View of the Title Compound. One disordered amine ligand has been omitted.

Figure 2. View of the Ca coordination sphere with amine ligands.

Structure of A Volatile magnesium β -Diketonato N,N,N',N' -tetramethylenethyldiamine Chelate $[\text{Mg}(\text{thd})_2(\text{N}_2\text{C}_6\text{H}_{16})]$	X7B
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I. Mutikainen, T. Hatanpaa, M. Leskela (Univ. Helsinki), A. Gualtieri (Univ. Modena) and J. Hanson (BNL)

In recent years there have been growing interest towards volatile -diketonates of alkaline earth, rare earth and transition metals. Reason for the interest is that these compounds can potentially be used as precursors in the preparation of oxide thin films by chemical vapor deposition (CVD). The main requirements for precursors used in CVD are high volatility and thermal stability. Both of properties are affected by the structure of the complex: monomeric and coordinatively saturated complexes are most volatile. If the -diketonate ligands do not saturate the coordination of the central metal, which is the case with alkaline earth metals heavier than Be, the coordination number will be fulfilled by oligomerisation or solvate molecule coordination. By adding different Lewis bases the coordination number can be fulfilled and oligomerisation and solvation molecule coordination avoided. The crystal structure of $\text{Mg}(\text{thd})_2\text{-N,N,N',N'}$ -tetramethylenethylenediamine was measured using synchrotron X-rays ($\lambda=1.0088$ Å) at 153 K using image-plates and off-line Fuji 2000 scanner. The complex was crystallized from 'super dry' ethylalcohol. The crystals are monoclinic, space group $P2_1/c$ (nr. 14), with $a=10.091(4)$, $b=19.133(5)$, $c=17.021(4)$ Å, $\beta=93.22(3)$ deg., $Z=4$, $R=0.072$ for 3072 reflections having $I>2\sigma(I)$. The coordination sphere of Mg is octahedral with two thd molecules coordinating to Mg via four oxygen atoms and the tetramethylenethylenediamine via both nitrogen atoms. The bond lengths in the Mg coordination sphere vary from 1.990(2) to 2.020(2) Å for Mg-O and 2.261(3) to 2.294(3) Å for Mg-N.

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Figure 1. View of the Title Compound.

Hydrothermal conversion of zeolites; an In-situ powder diffraction study. X7B

P. Norby, J.C. Hanson (BNL)

By using hydrothermal conversion of zeolites it is in some cases possible to synthesize materials which are otherwise impossible or difficult to obtain. The metastable nature of zeolites makes them suitable as starting materials. Especially conversion of one zeolite into another is of interest in order to obtain purer or novel zeolites. Hydrothermal conversion of zeolite Na-LTA has e.g. been used in the synthesis of pure and well crystalline zeolite Li-A(BW), $\text{LiAlSi}_4\text{O}_{14} \cdot \text{H}_2\text{O}$ (1).

In order to study the nature of hydrothermal conversion of zeolite LTA in detail an in-situ powder diffraction study has been performed. Hydrothermal conversions were performed at temperatures up to 260°C and pressures up to 45 atm. All syntheses were carried out in 0.5 or 0.7 mm quartz glass capillaries mounted in a ferrule. Pressure was applied from a cylinder of compressed nitrogen in order to maintain hydrothermal conditions. Time resolved powder diffraction patterns were collected using a Translating Image Plate System (TIPS) built especially for time- and temperature- and wavelength- dependent powder diffraction experiments at X7B. Figure 2 shows an example of time resolved powder diffraction data obtained during hydrothermal conversion of zeolite Na-LTA with an aqueous solution of LiCl at 260°C . The result in this experiment is actually a mixture of two zeolites; zeolite Li-A(BW) as the major product with minor quantities of a cancrinite type zeolite.

*This work was supported under contract DE-AC02-76CH00016 with the US Department of Energy by its Division of Chemical Sciences, Office of Basic Energy Sciences and by the Danish Natural Science Research Council.

Figure 1. Powder diffraction patterns obtained during hydrothermal conversion of zeolite LTA with aqueous LiCl at 260°C

Figure 2.

Carboxylation of alkali phenolates; an in-situ powder diffraction study. X7B

P. Norby, J.C. Hanson (BNL), M. Pink (U. Leipzig), R. Dinnebier, P. Stephens (SUNY, Stonybrook)

For more than 100 years it has been known that carboxylation of e.g. phenolates using carbon dioxide under pressure is possible(1,2). This so called Kolbe-Schmitt reaction is one of the most important industrial processes in the production of salicylic acid, a starting material for production of e.g. pharmaceuticals as aspirin. Although it is therefore a process of major industrial and economical importance, the mechanism of the reaction is still poorly known. Using the in-situ powder diffraction equipment(3) at X7B we have performed real time powder diffraction studies of the reaction at temperatures up to 150°C using CO_2 pressures up to 4 atm.

The in-situ experiments showed that even at room temperature sodium phenolate reacts with CO_2 and forms an disordered phase, which is probably a $\text{NaOC}_6\text{H}_5\text{-CO}_2$ adduct. Upon heating this is transformed into a well crystalline phase as shown in Fig. 1. This phase we succeeded in preparing on the diffractometer. A high resolution powder diffraction pattern was obtained at the beamline X3A1, and it was possible to determine the unit cell. The structure solution is in progress.

Upon further heating, the crystalline $\text{NaOC}_6\text{H}_5\text{-CO}_2$ phase decomposes, and the starting material reappears. At temperatures above ca. 140°C a new poorly crystalline phase is formed, probably another $\text{NaOC}_6\text{H}_5\text{-CO}_2$ phase. Upon prolonged heating conversion to poorly crystalline sodium salicylate was observed.

This work was supported by contract DE-AC02-76CH00016 with the US Department of Energy by its Division of Chemical Sciences, Office of Basic Energy Sciences and by the Danish Natural Science Research Council.

1. H. Kolbe, J. pr. Chem., 10, (1874) 98.

2. J. Schmitt, J. pr. Chem., 38, (1885) 397 3. P. Norby, "In-situ time resolved synchrotron powder diffraction studies of syntheses and chemical reactions." Presented at EPDIC IV, July 10-14 1995 in Chester. Materials Science Forum, Trans. Tech Publications Ltd.

Figure 1. In-situ X-ray Powder Diffraction diagrams of the carboxylation of sodium phenolate.

Figure 2.

SIEMENS SMART CCD DETECTOR APPLIED TO DIFFRACTION WITH SYNCHROTRON RADIATION FROM X7B AT NSLS

X7B

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The performance of A Siemens CCD detectors with a 2K chip was evaluated using radiation from bending magnet beamlines at SSRL and NSLS and from a rotating anode source with three type of optics. Also the goniometer was set up with the $\omega - 2\theta$ axis horizontal, with a fast shutter to allow for short and accurate exposures and with provision for incident beam monitoring by the data collection software. Wavelengths close to 1 Å were used exclusively. Data on lysozyme with Rsym of 7.2% to 1.5 Å was obtained in 5.5 hrs. Data on luciferase, which has a 302Åaxis was obtained in 8.0 hrs with Rsym of 13.6% to 3.4 Å. The system was also used for small molecule crystallography, solving a porphyrin, a zeolite and a carborane structure previously unsolved because of poor or small crystals. The system was also used for time-resolved powder diffraction and diffraction by multilayers on a macroscopic single crystal substrate. NSLS Data Sets:

Lysozyme: Unit cell dimensions $a=b=79.1$ $c=37.9$; Space group P43212 Frame width=0.15 deg. Frame time=15 sec.; 667 frames Total elapsed time= 5.5 hrs Total number reflections= 80875

Total unique = 19439 Rsym=7.2% to 1.5 Å 97.7% complete

Luciferase: Unit cell dimensions $a=59.9$ $b=112.7$ $c=301.8$; Space group P212121 Frame width=0.2 deg. Frame time=30 sec.; 660 frames

Total elapsed time=8.25 hrs Total number reflections=53825 Total unique = 26128 Rsym=12.9% to 2.7 Å; 86% complete

C7N1B10H15:

Unit cell dimensions $a=7.246$ $b=18.429$ $c=18.140$

=92.482 deg.; Space group P21/n Frame width=0.5 deg. Frame time=15 sec.; 720 frames (hemisphere of data)

Total elapsed time=6 hrs Total number reflections=5134 Total unique reflections=2153 Rsym=12.1% to 0.86 Å; 92.5% complete Solved by SHELXTL direct methods and refined to $R_1=0.068$

Sodalite: Unit cell dimensions $a=8.8465$

Space group Im-3m Frame width=0.5 deg. Frame time=45 sec.; 150 frames Total elapsed time=2.5 hrs Total number reflections=278 Total unique reflections=77

Rsym=7.2% to 0.891 Å; 100% complete Solved by SHELXTL direct methods and refined to $R_1=0.041$

Fe Silicide on Si(111): Sample with 10 overlayers shows diffraction peaks and thermal diffuse scattering in a "powder scan" of 400 frames, 15s and 0.1 deg. each.

The experiments at NSLS X7B were performed with Jonathan Hanson and members of the Catalysis group of the Chemistry Department at Brookhaven National Laboratory.

We thank Ivan Rayment of the Enzyme Institute of the University of Wisconsin, Madison for the lysozyme and luciferase crystals. William Clegg, University of Newcastle and Kenneth Wade, University of Durham provided the carborane crystal. The sodalite study was with Joseph Pluth, University of Chicago and R. Broach, UOP. The multilayer diffraction was with Peter Eng, University of Chicago.

The Adsorption of Hydrofluorocarbons and Hydrochlorofluorocarbons on Basic Molecular Sieves *

X7B

F. Poshni, C. P. Grey (SUNY Stony Brook), A. F. Gualtieri, P. Norby, J. C. Hanson (BNL), and D. R. Corbin (DuPont CR&D)

The syntheses of hydrofluorocarbons (HFCs), the environmentally friendly alternatives to the CFCs for refrigerant and blowing applications, are more complex than the syntheses of the CFCs and involve many more steps. Unwanted HFC and hydrochlorofluorocarbon (HCFC) isomers are often produced, and purification of the products remains a concern. For example, the isomer HFC-134 ($\text{CF}_2\text{HCF}_2\text{H}$) is a common byproduct during the synthesis of HFC-134a (CF_3CFH_2). Basic molecular sieves have been shown to be effective in separating a variety of HFC/HCFC gas mixtures [1]. We have been investigating the adsorption of HFC-134 and HFC-124a ($\text{CF}_2\text{HCF}_2\text{Cl}$) on zeolite Na-Y, to determine both how the gas molecules are bound to the zeolites, and whether there are any changes in the occupation and positions of the extra-framework cation sites.

Samples of dehydrated NaY were loaded with 32 molecules of HFC-134/HCFC-124a per unit cell, packed into 0.3 mm glass capillary tubes in a glove box and sealed. Diffraction experiments on both the loaded and bare zeolites were performed at room temperature and at 100 K. Data was collected with the Fuji Image Plate system, at a wavelength of 0.9338 Å, and showed significant changes between the bare (top) and HFC loaded samples (middle and bottom) in Figure 1. Structure refinements were performed using the GSAS and XRS-82 programs. The coordinates of the framework atoms and Na sites of Na-Y as a starting model for the bare zeolite were taken by Fitch et. al.[2]. Difference Fourier maps were used to locate the sodium and HFC positions. Electron density from the HFC molecules was observed at low temperatures in the supercages of the zeolite. Rigid body constraints were initially imposed for the modelling and localization of the HFC molecule.

- [1] D. R. Corbin and B. A. Mahler, W.O. 94/02440 (February 3, 1994).
[2] A.N. Fitch, H. Jobic, H. Renouprez, J. Phys. Chem., 90, 1311 (1986).

Figure 1.

* NSF grant DMR-9458017 and DE-AC02-76CH00016 US DOE by its Division of Chemical Sciences, Office of Basic Energy Sciences and by the Danish Natural Science Research Council.

Reflectance Calibrations of AXAF Witness Mirrors in the Ir M-edge Region *	X8A
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D.E. Graessle, J.J. Fitch, B. Harris, J.P. Cobuzzi, D.A. Schwartz (SAO), R.L. Blake (LANL)

Systems and procedures have been completed for reflectance calibrations of witness mirrors to the coatings of flight optics of NASA's Advanced X-ray Astrophysics Facility (AXAF) in the 2-6 keV range on NSLS Beamline X8A. This energy range includes the M-absorption edges for iridium, the coating material for AXAF. The flight optics and associated witness mirrors are being coated, and completion of all eight elements and the 40 synchrotron witness mirrors is expected by February 1996. The X8A calibrations will be completed by Launch Date, in September 1998. Each mirror requires approximately four to five days of run time to calibrate in full detail. This detail includes angle scans at eight energies for alignment and layer modeling purposes, and eight energy scans at fixed grazing angle covering the full range. The required grazing angles are all less than 1.5 degrees. The energy detail is as broad as 25 eV in the continuum range above 3500 eV, but is as narrow as 1 eV in the troughs of the M-edges, where such detail is necessary to specify the reflectance accurately. Approximately 400 energy points are included in the energy scans.

The iridium shows certain unique spectral features, including more extended XAFS than we have seen on either gold or platinum mirrors, which we have studied previously on this beamline. The M_V and M_{IV} absorption edge troughs appear at 2080 eV and 2156 eV respectively, some 40 eV higher than the tabulated electron binding energies typically published for iridium (e.g. Bearden and Burr, Rev. Mod. Phys. 1967). We discovered similar results for the M_V and M_{IV} absorption edges for gold and platinum. The displacement of these edges may be the result of a slow onset of the absorption due to the behavior of the density of states, most recently calculated for gold by A. Owens et al. (submitted to Ap. J. Lett. 1995). The AXAF spectroscopic devices, including the AXAF CCD Imaging Spectrometer (ACIS) and the High-Energy Transmission Grating Spectrometer (HETGS), will require the energy detail provided by our calibrations to meet the mission's scientific goals. In addition, certain elements of the ACIS and the HETGS are being calibrated in part at NSLS through collaboration with us.

Information on the repeatability and uniformity of the coatings, and the level of molecular contamination, will be available soon, as work continues to calibrate more of the 40 witness mirrors. The reflectance at the M-absorption edges is significantly affected by molecular contamination, as we have reported previously.

Optical constants from transmission and reflection measurements	X8C, X8A
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R.L. Blake(LANL), B.H. Harris, J.J. Fitch, D.E. Graessle, and D.A. Schwartz(SAO)

A program is underway to measure foil transmissions and mirror reflectivities of suitably prepared samples. By application of the Fresnel equations and Kramers-Kronig relations to terms derived from the measurements one can obtain both the real and imaginary parts of the complex dielectric constant for the material, which may be an element or compound and in any state. At the energies accessible on X8C/A(1-15 keV)chemical binding effects are small or can be accounted for. A reflectometer test station (RTS) with one arc sec angular accuracy and capable of routine operation in ultra-high vacuum is used for both transmission and reflection measurements in this program, and also serves other users for efficiency measurements of transmission gratings, reflection gratings, multilayer gratings, windows, detectors, etc.

Improvements in the x-ray ring stability made over the last year by NSLS scientific and technical staff now allow our 0.1 percent precision measurements to yield optical constants with one percent accuracy in many cases. Over the last two years we have measured:

1. Ir reflectivity versus energy and angle over the M-edge region (2000-3500eV)
 2. Mo reflectivity of single crystal, polycrystalline, secondary- recrystallized single crystals, and evaporated samples(at 5 and 10 keV).
 3. Ir, Pt, and Au foil transmissions versus energy over M- and L-edge regions.
- New data on Pt and Au will permit optical constants n and k to be determined as accurately as the thickness can be measured-our primary limitation for transmission measurements. For reflectivity data the primary limitation is from surface surface roughness. Both of these factors are to be improved through collaborations in future work. New data for Ir in both reflection and transmission are the only data available from measurements over the M- and L- edge regions.

* Supported by NASA (NAS8-40224) and the US DOE.

AXAF Synchrotron Calibrations of Ir-coated Witness Mirrors over 5-12 keV *	X8C
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D.E. Graessle, J.J. Fitch, B. Harris, J.P. Cobuzzi, D.A. Schwartz (SAO), R.L. Blake (LANL)

Reflectance calibrations of witness mirrors to the coating processes for AXAF (Advanced X-ray Astrophysics Facility) flight optics are proceeding rapidly on NSLS Beamline X8C. To date, 10 mirrors have been calibrated, including at least two mirrors from each of the innermost three elements to be flown. The remaining elements will be coated within the next four months. Approximately 30 mirrors will be calibrated in the X8C range, with varying degrees of detail.

X8C provides the most sensitive test of the uniformity and repeatability of the AXAF coating processes, because it covers the upper end of the full 50-12,000 eV calibration range. Angular accuracy down to one arc second is required at 10 keV because of the steepness of the iridium critical angle cut-off at that energy. The critical angle at 10 keV is approximately 27.4 arc minutes, which is also the mean grazing angle of AXAF's innermost mirror pair. Therefore an accurate calibration will be required through this energy and angle range. Beamline X8C together with our reflectometer perform remarkably well at maintaining this angular certainty under normal operations. Notwithstanding, significant improvement is expected with the use of the new NSLS Digital Feedback Stabilization system in the near future.

Calibration efforts have reduced the time required per mirror to approximately 2.3 days, including operator and storage ring overheads, excluding accidental beam dumps.

The coating process, which must be completed twice for each element to produce the required witness mirrors, is quite reproducible, indicating that we may be able to reduce the amount of data and operational detail required in future measurements. Mirrors coated in separate processes have been shown to be consistent within about 1 - 1.5% in all cases excluding the interference fringes. This implies that the coating density is very uniform and reproducible from coating run to coating run. Using a Fresnel equation model with uniform layer thicknesses and a modified Debye-Waller roughness factor, we are able to fit the AXAF witness mirror reflectance data to within 1% relative residuals for optical constants and layer thicknesses. The optical constants are very similar to those published by Henke et al. (Atomic Data and Nuclear Data Tables, 1995) if we assume a 1.5% decrement in the coating density below bulk for iridium. The calibration is therefore within its error budget requirements, and we are now well on our way to completing a calibration of AXAF over 5-12 keV within 1% relative error and with full energy detail.

* Supported by NASA (NAS8-40224) and the US DOE.

THE USE OF SYNCHROTRON RADIATION IN THE CALIBRATION OF AXAF 5-12 keV *	X8C
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D.E. Graessle, J.J. Fitch, B. Harris, J.P. Cobuzzi, D.A. Schwartz (SAO), R.L. Blake (LANL)

During the past five years, significant efforts have been made to develop systems and procedures for calibration of NASA's Advanced X-ray Astrophysics Facility (AXAF) using synchrotron radiation. The goal for the calibration is to provide AXAF mirror efficiency versus energy within 1% relative error over the 50-12,000 eV energy range. AXAF has four pairs of nested Wolter Type I mirrors, which are internally-reflecting conic sections. As planned, witness mirrors to the coating processes for each of the AXAF flight mirrors would be brought to the synchrotron for calibration of reflectance versus energy and angle. The X8C beamline provides the upper range for the calibration, specifically 5-12 keV. Some thirty mirrors in all must be calibrated in this energy range. The mirror coatings are approximately 300 Å of iridium over a 100 Å chromium binding layer on Zerodur substrates. Scans of reflectance versus energy and angle would be required, and would be analyzed for optical constants and coating layer thicknesses using a Fresnel equation model. The critical grazing angle for iridium above 5000 eV is less than one degree.

The systems and procedures to be used on X8C are essentially completed. We have obtained reflectance measurements in the 5-12 keV range with acceptable accuracy and precision. Using the Fresnel model with uniform layer thicknesses and a modified Debye-Waller correction for scatter due to microroughness, we are able to fit reflectance versus angle of incidence down to 1% values of R with less than 1% relative residuals. Calibration of a mirror may be completed in a three-day period with normal operations and infrequent beam dumps.

Sample-to-beam alignments are critical to the accuracy of the data. At 10 keV, the critical angle cut-off is quite steep, so that an angular error of one arc second produces a one-percent error in reflectance, which exceeds the error budget allowance. Our X8C studies have shown that this degree of angular accuracy is usually attainable in our system. The reflectometer operates with a horizontal plane of incidence, the p-polarization plane at a synchrotron.

Calibrations of witness coupons to the actual flight optics are in progress.

* Supported by NASA under NAS8-40224 and by the US DOE.

Manipulating mesophase behavior of hydrated DHPE: An x-ray diffraction study of temperature and pressure effects.	X9A, X9B
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M. Caffrey (Ohio State University)

A pressure-temperature phase diagram for 1,2-dihexadecyl-sn-glycerol-3-phosphoethanolamine (DHPE) in 50 of 1 to 1,200 bar and 65 to 90 C. The lamellar gel (Lb') phase prevails at high pressure and low temperature. It gives way successively to the lamellar liquid crystalline (La) and inverted hexagonal (HII) phases as pressure is lowered and temperature is raised. Measurements were made using synchrotron-based x-ray diffraction and a high pressure beryllium cell. The pressure-dependence of the Lb'/La transition temperature, dT_m/dP , is 25.2 C/kbar. Compression/expansion in the lamellar phases was highly anisotropic. The isothermal pressure-dependence of the chain packing and lamellar repeat distance, $(d/P)T$, in both the La and Lb' phases was insensitive to temperature in the range studied. The average $(d/P)T$ value for the lamellar repeat in the La and Lb' phases and for the chain packing repeat in the Lb' phase is 3.001, 1.18006, and -0.117004 /kbar, respectively. In like manner, the isobaric temperature-dependence of the chain packing and lamellar repeat distance, $(d/T)P$, in both the La and Lb' phases is insensitive to pressure in the range studied. The average $(d/T)P$ value for the lamellar repeat in the La and Lb' phases and for the chain packing repeat in the Lb' phase is -0.1540005, -0.0530003, and 0.004300002 /C, respectively. The absolute value of the ratio of the isothermal pressure- and isobaric temperature-dependence of all structure parameters measured, including area per chain, is remarkably close to the dT_m/dP value reported above. A careful evaluation of mesophase structure parameters, one-dimensional electron density profile and wide-angle diffraction profile has enabled us to describe in considerable detail the structure response of the Lb' phase in hydrated DHPE to temperature and pressure. Problems that can arise due to x-ray damage were evaluated.

XAFS Studies of the Zinc Storage Protein of <i>Xenopus laevis</i> Oocytes	X9B
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David S. Auld, Ke Zhang (Biostructures Institute), Marcello Montorzi, Kenneth H. Falchuk & Bert L. Vallee (Harvard Med. Sch.)

X. laevis vitellogenin is a zinc protein containing 1 g at of zinc per mol of protein of MW 220,000 (1). It is a central component of a zinc distribution system that is involved in a) zinc transfer from liver to oocyte sites b) zinc storage in unfertilized eggs and c) zinc exchange from storage molecules to apoproteins in the embryo. The basic protein unit in yolk platelets is derived from the proteolytic processing of vitellogenin. The vitellogenin cleavage products phosvitin and lipovitellin remain associated with each other in a microcrystalline state in the yolk platelets. The purified lipovitellin contains 1 g at of Zn per mol of protein while the phosvitin contains none (1). Our initial XAFS studies have been directed toward the examining Zn in yolk platelets and purified vitellogenin and lipovitellin.

The XAFS spectra of the vitellogenin, yolk platelet suspension and solid lipovitellin are essentially identical (2). The results show the Zn is bound to 4.0 N/O at 1.98 Å. The XAFS spectrum of a suspension of yolk platelets with a zinc concentration of about 1 mM differs from yolk platelets solubilized in 1 M NaCl, pH 7.5 (Fig. 1) while the spectra for yolk platelets and lipovitellin dissolved in 1 M NaCl are essentially identical (Fig. 2). Analyses of these spectra indicate the Zn is bound to 4 N/O atoms at 1.98 Å in the microcrystals of the yolk platelets but has a Cl ion or S atom coordinated to the zinc in the NaCl solubilized states of both the yolk platelets and the purified lipovitellin. These results suggest one of the N/O ligands in the crystalline suspension of the yolk platelets may be a water molecule that is displaced most likely by a chloride ion in the solution state.

1. Montorzi, M., Falchuk, K. H., & Vallee, B.L. Biochemistry 34, 10851-10858, 1995.

2. Auld, D. S., Zhang, K., Montorzi, M., Falchuk, K. H., & Vallee, B.L. in preparation.

Figure 1. XAFS spectra for yolk platelet suspension (circles) and solubilized in NaCl (line).

Figure 2. XAFS spectra of yolk platelets (circles) and lipovitellin (line) solubilized in NaCl.

* Supported by NIH grant GM-47534.

TIME-RESOLVED X-RAY SPECTROSCOPY OF HEMEPROTEINS : NOVEL METHODS OF DATA ACQUISITION AND ANALYSIS APPLIED TO MBCO RELAXATION PHENOMENA

X9B

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Time-resolved x-ray structural data has become feasible based on the high flux and brightness of synchrotron X-Ray beams. One of the most closely examined problems in this area of time-resolved structure determination has been the examination of intermediates in ligand binding to myoglobin. Recent crystallographic experiments using synchrotron radiation have identified the protein tertiary and heme structural changes that occur upon photolysis of the myoglobin-carbon monoxide complex (Schlichting et al. Nature, 371, p.808 (1994)). However, the precision of protein crystallographic data (~ 0.2 Å) is insufficient to provide precise metrical details of the iron-ligand bond lengths. Using time-resolved x-ray data acquisition techniques on microsecond to millisecond timescales along with simulations based on the ab initio Extended X-Ray Absorption Fine Structure code FEFF 6.01, we analyzed data taken on photolyzed solution samples of the myoglobin-carbon monoxide complex from 10- 260 K. We provide precise metrical details for the Mb*CO state at 10 K and structural information based on x-ray edge data for microsecond and longer time relaxations above the glass transition.

An XAS Study on CO Adducts of [NiFe] Hydrogenases

X9B

Zhijie Gu*, Suranjan B. Choudhury*, Christian B. Allan* and Michael J. Maroney** (*Department of Chemistry and **Program in Molecular and Cellular Biology, University of Massachusetts, Amherst, MA 01003)

Our work is directed at understanding the catalytic mechanism of the hydrogenases (H_2 ase) and what role(s) the Ni center plays in Ni-containing enzymes. The crystal structure of the H_2 ase from *D. gigas* reveals a heterodinuclear [NiFe] site, where the metals are bridged by two cysteinate ligands. One potential role of the Ni site is as a substrate/inhibitor binding site. In order to investigate this, we have examined the structure of a CO adduct of *Chromatium vinosum* H_2 ase and its photoproduct by using XAS.

Carbon monoxide is a competitive inhibitor of reduced forms of [NiFe] H_2 ases. Both the H_2 reduced and CO-bound enzymes are light sensitive, a property that is related to photodissociation of a ligand. The photodissociation is reversible upon annealing the sample at 200 K, and therefore provides a mechanism for studying the structure with CO on or off the protein. The edge obtained from the CO adduct and its photoproduct are shown in Figure 1. The figure shows that the loss of CO is accompanied by a very small (0.5(2) eV) shift in the edge energy that is reversible. The XANES spectrum contains features that are sensitive to the geometry/coordination number of the Ni. The spectra for the CO adduct and its photoproduct do not reveal a $1s \rightarrow 4p_z$ transition that is diagnostic for a four-coordinate planar environment. A peak assigned to a $1s \rightarrow 3d$ transition is observed (Figure 1). This feature does not show a change that corresponds to the presence or absence of CO, and has an area that is most with a six-coordinate environment.

The analysis of the EXAFS spectra are summarized by Figure 2. For the CO adduct the data are best fit by a combination of 4 S @ 2.240(1) Å + 1 Fe @ 2.618(3) Å, and for the photoproduct the best fit is for 4 S @ 2.240 (1) Å + 1 Fe @ 2.564(4) Å (using a backtransform window of 1.1-2.6 Å). These fits suggest only a slight modification of the Ni-Fe distance, the change that is indicated by difference spectra as well. These results provide no evidence for a CO ligand bound to Ni center, but are consistent with CO binding to the Fe site.

Figure 1. Ni K-edge XANES spectra of the CO adduct of *Chromatium vinosum* hydrogenase and its photoproduct.

Figure 2. Ni K-edge EXAFS spectra and fits of the CO adduct of *Chromatium vinosum* hydrogenase and its photoproduct.

* This research was supported by grants from NIH HL-45892 and RR-01633 and NSF BIR-9303830.

Structural Studies of Discotic Liquid Crystals

X9B

P. A. Heiney, S. Ghosh, N.C. Maliszewskyj (Penn), and Philippe Henderson (Shell Research, Belgium)

We have used grazing incidence x-ray diffraction (GID) to characterize a series of Langmuir-Blodgett films of mono- and bi-functionalized triphenylene derivatives. At the air-water interface, the molecules are oriented "edge-on" to the interface, and are presumed to pack cofacially. This orientation is preserved upon transfer to a solid substrate. The resulting multilayer films are lamellar, with the constituent disks organizing into columns aligned along the axis of deposition. The attachment of terminal hydroxyl groups to the aliphatic substituents of the disks results in the development of correlations between layers and distinct tilts (approximately 40 degrees) of the disks with respect to the layer normal. Within the plane of the film, measured d-spacings larger than the nominal size of the disks may be attributed to superlattice ordering of tilts of the molecules with respect to the column axis. The in-plane order is best characterized as "liquid-crystalline" with evidence of paracrystalline disorder. On heating, the films exhibit an irreversible phase transition to a state resembling the bulk Dhd phase, in which the disks are still organized in columns with no intracolumnar tilt.

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EXAFS and XANES Studies of Nitrile Hydratases

X9B

Mark J. Nelson, John G. Cummings (DuPont), Lewellyn Durney, Daihung Duong, and Robert C. Scarrow (Haverford College)

Nitrile hydratases are metalloenzymes that catalyze the hydration of nitriles to amides. We are studying two classes of these - those that contain low-spin Fe^{3+} and those that contain low-spin Co^{3+} . A subset of the iron nitrile hydratases is expressed in an inactive form and activated by light. We are studying the metal coordination environments of examples of each of these classes as part of a program to elucidate the chemical mechanisms of light activation and nitrile hydration. We have shown that the iron nitrile hydratases have a biologically novel $\text{N}_3\text{S}_2\text{O}$ coordination with three histidines, two cysteines, and a hydroxide. The Fe-S bonds are slightly shorter at pH 9 (where the enzyme is inactive) than at pH 7, explaining dramatic differences in the Fe-S region of resonance Raman spectra. Subtle changes in the Fe-S bonds are also seen in the presence of inhibitors. We have collected data for the cobalt enzyme and a series of model complexes. Preliminary analysis suggests that the novel $\text{N}_3\text{S}_2\text{O}$ coordination is preserved in this class of nitrile hydratase, as expected based on amino acid sequence homologies. This confirms that the cobalt nitrile hydratase is a cobalt-sulfur protein, the first, we believe, to be characterized.

Metal Cluster Active Sites in Proteins

X9B

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In the past decade we have investigated a number of metalloproteins containing nonheme-iron centers. This class includes catechol 2,3-dioxygenase (2,3-CTD), purple acid phosphatase, methane monooxygenase, and stearyl desaturase.

1) We have obtained and analyzed data for 2,3-CTD and its substrate complexes. A 5-coordinate iron site with an average Fe-ligand distance of 2.09 Å is found in the isolated protein; catechol binding elicits a new short bond at 1.93 Å, which is proposed to be the oxygen from the deprotonated hydroxyl group of the coordinated catecholate monoanion. This work has been published [1].

2) We have collected and analyzed data on the Fe(III)Zn(II) derivative of the purple acid phosphatase from porcine uterus which allows us to look at the Fe(III) and the Zn(II) sites separately. In the phosphate complex of this derivative, the observation of Fe-Zn and M-P (M = Fe, Zn) distances of 3.3 and 3.2 Å, respectively, indicates an FeZn(OR)₂ core structure with phosphate bound to the metal center in a bridging mode. This paper is in preparation.

3) Data was also collected on methane monooxygenase from *Methylosinus trichosporium* OB3b, in which an Fe-Fe separation of 3.0 is observed which we associate with an Fe₂(OR)₂ diamond structure, consistent with the crystal structure of the enzyme from *Methylococcus capsulatus* (Bath) taken at -160°C [2].

4) Stearyl ACP Δ⁹ desaturase is the newest member of this class of proteins and its data is currently being analyzed. With the crystallographic data available for hemerythrin, ribonucleotide reductase and the hydroxylase component of methane monooxygenase, kidney bean phosphatase, and EXAFS data for the other proteins, we will be able to identify the common structural features that make up these dimetallic sites within this class and to discern the variations in structure that control mechanism and function.

5) We have also examined the EXAFS of model complexes related to intermediates of these iron proteins; these results are published [3-5]. Data was also taken and analyzed on copper model complexes modeling the copper dioxygen chemistry in metalloproteins, and this paper is published [6]. In two cases, the EXAFS analysis has been crucial for the structure determination of these unstable model complexes.

[1] Shu, L., Chiou, Y.-M., Orville, A. M., Miller, M. A., Lipscomb, J. D., Que, L. Jr. *Biochemistry* 34: 6649-6659 (1995).

[2] Rosenzweig, A. C., Nordlund, P., Takahara, P. M., Frederick, C. A., Lippard, S. J. *Chemistry & Biology* 2: 409-418 (1995).

[3] Kitajima, N., Tamura, N., Amagai, H., Fukui, H., Moro-oka, Y., Mizutani, Y., Kitagawa, T., Methur, R., Heerwegh, K. Reed, C. A., Randall, C. R., Que, L. Jr., Tatsumi, K. *J. Am. Chem. Soc.* 116: 9071-9085 (1994).

[4] Randall, C. R., Shu, L., Chiou, Y.-M., Hagen, K. S., Ito, M., Kitajima, N., Lachicotte, R. J., Zang, Y., Que, L. Jr. *Inorg. Chem.* 34: 1036-1039 (1995).

[5] Dong, Y., Fujii, H., Hendrich, M. P., Leising, R. A., Pan, G., Randall, C. R., Wilkinson, E. C., Zang, Y., Que, L. Jr., Fox, B. G., Kauffmann, K., Mnck, E. J. *Am. Chem. Soc.* 117: 2778-2792 (1995).

[6] Mahapatra, S., Halfen, J. A., Wilkinson, E. C., Pan, G., Cramer, C. J., Que, L. Jr., Tolman, W. B. *J. Am. Chem. Soc.* 117: 8865-8866 (1995).

EXAFS of *Azotobacter vinelandii* Nitrogenase Iron Protein: MgATP does not Disrupt the [4Fe-4S] Cluster *

X9B

R. C. Scarrow, N. Taufen (Haverford College), L. C. Seefeldt, and W. N. Lanzilotta (Utah State University)

Previous studies have suggested that MgATP or MgADP binding to the nitrogenase iron protein (FeP) induces protein conformational changes which control component docking, intercomponent electron transfer and substrate reduction. Resonance Raman and CD spectra suggest that MgATP binding to oxidized FeP may partially convert the [4Fe-4S]²⁺ cluster to [2Fe-2S]⁺ clusters (Fu, W. G., Morgan, T. V., Mortenson, L. E., and Johnson, M. K. (1991) *FEBS Lett.* 284, 165-8). To test this, we measured the Fe K-edge XAS of frozen (30K) oxidized FeP in the presence and absence of MgATP, and find no significant changes in either the edge or EXAFS spectra, which resemble those of a model [4Fe-4S] complex (Figure 1).

Edges were modelled identically for the two protein samples: 75% Gaussian/25% Lorentzian edge centered at 7119.5 eV with width 7.2 eV, and Gaussian pre-edge peaks at 7112.4 and 7119.1 eV (FWHM = 2.3 and 3.7 eV; areas = 0.27 and 0.6 eV × edge height). The best EXAFS fits have 4 or 5 sulfur scatterers (r_{FeS} = 2.28 Å) and 3 iron scatterers (r_{FeFe} = 2.72 Å) per iron. Assuming disorder is the same for both samples, the refined number of Fe-Fe scatterers are very similar; with $\Delta\sigma^2$ = 0.001 Å², n = 3.24(6) and 3.12(6) in the absence of presence of MgATP.

The similarities of the XAS and the EXAFS analyses indicate that the iron in oxidized FeP is in a [4Fe-4S]²⁺ cluster with and without added MgATP. These results extend earlier findings of no XAS-detectable changes in the [4Fe-4S]¹⁺ cluster upon addition of MgATP to reduced FeP (Lindahl, P. A., Teo, B. K., and Orme-Johnson, W. H. (1987) *Inorg. Chem.* 26, 3912-6). They also support recent CD results for oxidized FeP bound to nucleotides (Seefeldt, L. C., Ryle, M. J., Lanzilotta, W. N., Scarrow, R. C., and Jensen, G. M., *J. Biol. Chem.* (1996), 271, 1551-7).

Figure 1. Baseline corrected and normalized Fe K-edge XAS of FePox in the absence (thin line) or presence (thick line) of MgATP, and of [(CH₃)₄N]₂[Fe₄S₄(SPh)₄] (dots). a) Edge; successive spectra are offset by 0.1. b) EXAFS.

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STRUCTURE-FUNCTION OF COBALAMIN DEPENDENT EN- ZYMES: X-RAY ABSORPTION STUDIES ON METHIONINE SYNTHASE FROM E. COLI *	X9B
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The first crystallographic data on an enzyme bound cobalamin cofactor, methylcobalamin bound to the 27 kDa fragment of methionine synthase from E. coli (Drennan, C. L. et al. Science, 1994, 266, 1669) revealed dramatic changes in the structure of the cofactor upon enzyme binding. The most striking change is that the 5,6-dimethylbenzimidazole (DMB) group of the cofactor is displaced and replaced by a His group of the enzyme. The DMB base with the sugar phosphate linkage penetrates into a deep pocket of the enzyme to stabilize enzyme binding. His759 of the enzyme, bound to the Co atom, is part of a hydrogen bonding network involving Asp757 and Ser810 residues. Examination of different mutants, affecting the three catalytically important residues, His759, Asp757, Ser810, provides insights into how the enzyme controls the Co-C bond cleavage. X-ray edge results on the Co(II) form of mutant H759G shows that replacing His759 with a Gly residue causes the formation of a four-coordinate species with no Gly ligation to the Co. The Co(II) form of mutant D757E, in which Asp757 is replaced by Glu, indicates similar geometry to that of the wild-type Co(II). Both mutants have edge positions at lower energies indicating higher electron density on the Co(II) form of mutant H759G shows that replacing His759 with a Gly residue causes the formation of a four-coordinate species with no Gly ligation to the Co. The Co(II) form of mutant D757E, in which Asp757 is replaced by Glu, indicates similar geometry to that of the wild-type Co(II). Both mutants have edge positions at lower energies indicating higher electron density on the Co with respect to the wild-type Co(II) form.

X-ray Absorption Spectroscopy Comparison of the Active Site Structures of Phanerochaete chrysosporium Lignin Peroxidase Isoenzymes H2, H3, H4, H5, H8, and H10 *	X9A, X9B
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R. Sinclair, B. Copeland, I. Yamazaki, and L. Powers(National Center for the Design of Molecular Function, Utah State University)

The iron heme and its immediate environment can provide information that is pivotal to our understanding of the structural and mechanistic features that confer unusual properties to the heme peroxidases. X-ray absorption spectroscopy (XAS), which is ideally suited for the investigation of the local environment and electronic structure of the heme iron of heme proteins, has been used to characterize a variety of lignin peroxidase and manganese-dependent peroxidase isoenzymes produced by the white rot fungus *Phanerochaete chrysosporium*. The data suggest no differences within the error in the first coordination shell of iron for the isoenzymes H2, H3, H4, H5, H8, and H10 examined in this study. The pyrrole nitrogens are at a distance of 2.05 [0.015] Å, the proximal histidine nitrogens are at 1.93 [0.02] Å, while the sixth ligands are located at 2.17 [0.03] Å. Significant differences are observed in higher coordination shells which may be related to differences in conformational differences in the heme.

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* NIH RR-01633

Structural Characterization of the Effects of Halide Inhibition on Mn Catalase *

X9B

Timothy L. Stemmler and James E. Penner-Hahn (University of Michigan)

Manganese catalase, isolated from *Lactobacillus plantarum*, is a dinuclear Mn protein which catalyzes the disproportionation of H_2O_2 to O_2 and H_2O , cycling between Mn(II)/Mn(II) and Mn(III)/Mn(III) [1]. If the reduced enzyme is incubated in the presence of peroxide, the final product contains a 60:40 mixture of the Mn(II)/Mn(II) and Mn(III)/Mn(III) forms. In contrast, incubation of either the oxidized or the reduced enzyme with peroxide in the presence of inhibitory concentrations of fluoride converts the enzyme entirely to the Mn(II)/Mn(II) form [2].

Halide inhibition of Mn catalase is pH dependent, with stronger inhibition occurring at lower pH values. However, EXAFS data (see Figure) demonstrate that pH alone has no significant effect on the Mn_2 core structure. In contrast, incubation in the presence of halides and peroxide results in a change to a more symmetric Mn-nearest neighbor environment.

The native enzyme has extremely weak outer shell scattering [3], suggesting relatively few imidazole ligands and no detectable Mn...Mn interaction. However, when the enzyme is inhibited with fluoride, a new peak, attributable to a Mn...Mn interaction at 3.5 Å, appears (see Figure). In model compounds the detection of long range metal...metal interactions in EXAFS generally reflects the presence of multiple bridging ligands between the metals [4]. Thus, fluoride inhibition may result in formation of an additional bridging ligand, such as F^- or OH^- . This provides the first direct structural data for the fluoride inhibited enzyme. Detailed analysis of these data is in progress.

[1] Penner-Hahn, J. E. In *Manganese Redox Enzymes*; V. L. Pecoraro, Ed.; VCH Publishers, Inc.: New York, 1992; pp 29-45. [2] Waldo, G. S.; Penner-Hahn, J. E. *Biochemistry* 1995, 34, 1507-1512. [3] Waldo, G. S.; Yu, S.; Penner-Hahn, J. E. *J. Am. Chem. Soc.* 1992, 114, 5869-70. [4] Riggs-Gelasco, P. J.; Stemmler, T. L.; Penner-Hahn, J. E. *Coord. Chem. Rev.* 1995, in press.

Figure 1. Fourier transforms for reduced Mn catalase.

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XAS of Rat Liver Arginase. Characterization of the Mn_2 Core During Catalase Turnover *

X9B

T. Stemmler, J. Penner-Hahn (Univ Michigan), D. Ash and T. Sosson (Temple Univ)

Arginase catalyzes the hydrolysis of arginine to ornithine and urea. As arginine is the substrate for NO synthase (NOS), arginase may be important in regulating NOS activity. Rat liver arginase contains a dinuclear Mn active site [1] and is thus similar in structure to other dinuclear metalloproteins, including Mn catalase. Consistent with this structural similarity, arginase has recently been found to catalyze (slowly) the disproportionation of H_2O_2 [2]. We previously reported EXAFS and XANES for Mn catalase [3-4]. Here we describe recent extensions to include arginase. The ultimate goal of this work is to establish the features that distinguish the arginase and catalase active sites.

Recently it has been found (Ash & Sosson, unpublished results) that the addition of H_2O_2 in the presence of ornithine gives an initial burst of O_2 production, followed by slow, irreversible inactivation of the catalase activity. The XANES (not shown) indicate that the Mn remains Mn(II). This is in contrast to the behavior of Mn catalase, where addition of H_2O_2 gives a mixture of Mn(II) and Mn(III) [4]. The absence of significant change in the XANES spectra suggests that the ornithine + inactivation does not result in any significant change in the local environment of the Mn in arginase. In contrast, there is a significant change in the EXAFS spectrum of the inactivated enzyme (see Figure).

There is no significant Mn...Mn peak in the spectrum for native arginase. However, a new peak appears at a distance corresponding to a Mn-Mn distance of ca. 3.4 Å following inactivation, suggesting that there has been a significant change in the dinuclear Mn site.

[1] Reczkowski, R. S.; Ash, D. E. *J. Am. Chem. Soc.* 1992, 114, 10992-4. [2] Khangulov, S. V.; Pessiki, P. J.; Barynin, V. V.; Ash, D. E.; Dismukes, G. C. *Biochemistry* 1995, 34, 2015-2025. [3] Waldo, G. S.; Yu, S.; Penner-Hahn, J. E. *J. Am. Chem. Soc.* 1992, 114, 5869-70. [4] Waldo, G. S.; Penner-Hahn, J. E. *Biochemistry* 1995, 34, 1507-1512.

Figure 1. FT before and after inactivation with ornithine+ H_2O_2 .

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XAS OF SUPEROXIDE DISMUTASE. USE OF A SAGITTALLY FOCUSED BEAM TO AVOID PHOTOREDUCTION *

X9B

D.Tierney, J.Penner-Hahn (Univ of Michigan), and F. Yamakura (Juntendo Univ)

Superoxide dismutase (SOD) catalyzes the disproportionation of superoxide to H_2O_2 and O_2 while cycling between an oxidized and a reduced state. The Fe and Mn SODs constitute a family of closely related proteins [1], having homologous folding patterns and complete conservation of metal ligation. Despite this similarity, Mn and Fe are not necessarily interchangeable. If the *Thermus thermophilus* or *E. coli* MnSODs are reconstituted with Fe, the resulting protein is inactive [2]. Similarly, the *Pseudomonas ovalis* FeSOD loses activity when reconstituted with Mn [3].

In order to compare, at high resolution, the structures of the Fe and Mn enzymes and to determine the structure of the enzyme when substituted with the "wrong" metal [4], we have undertaken EXAFS measurements of FeSOD [5], and native and Fe substituted MnSOD. The latter are limited by the sensitivity of the MnSOD to photoreduction. In contrast to the Fe enzyme, where photoreduction is relatively slow [5], Mn(III)SOD and Fe(III) substituted MnSOD suffer extremely fast photoreduction, giving > 50% reduction in ca. 10 hours at 40K.

To avoid photoreduction, we used the sagittally focused beam at X9-B to focus the incident x-rays to a small spot and translated the sample horizontally at the end of each scan. Recent measurements (see Figure) confirm the utility of this approach. The difference XANES spectra for conventionally measured data show clear evidence for photoreduction. In contrast, there is no detectable photoreduction for the data measured using the sagittally focussed beam. Analysis of these data is in progress.

[1] Stallings, W.; Patridge, K.; Strong, R.; Ludwig, M. J. Biol. Chem. 1984, 259, 10695-9. [2] Yamakura, F.; Suzuki, K. J. Biochem. (Tokyo) 1980, 88, 191-6. [3] Ose, D.; Fridovich, I. Arch. Biochem. Biophys. 1979, 194, 360-4. [4] Yamakura, F.; Matsumoto, T.; Terauchi, K. Free Radical Res. Commun. 1991, 13, 329-34. [5] Tierney, D.; Metzger, A.; Ludwig, M.; Penner-Hahn, J. Biochemistry, 1995, 34, 1661-1668.

Figure 1. Difference XANES spectra relative to first scan. A) Conventional B) Measured as described in text. Elapsed time ca. 16 hours in each case.

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Structure of Binary and Ternary Complexes of Zinc and Cobalt Carboxypeptidase A as Determined by XAFS *

X9B

Ke Zhang (Biostructures Institute) and David S. Auld (Harvard Med. Sch.)

Carboxypeptidase A, ZnCPD, is typical of a wide range of exo and endometalloproteases that have 3 protein ligands and a water molecule bound to a catalytic Zn atom. Such enzymes generally have bell-shaped pH-activity profiles ($EH_2 \leftrightarrow EH \leftrightarrow E$) where the concentration of the catalytic species EH is regulated by pK_{EH_2} and pK_{EH} .

This XAFS study has determined the structure and pH behavior of binary and ternary product complexes of CPD A in order to examine the role of the Zn-bound water in catalysis. Increasing the pH from 7 to 10 of its L-Phe complex results in the same type of progressive changes in the near-edge XAFS spectrum as is seen for ZnCPD (1) but the changes are complete by more than 1 pH value below that observed for ZnCPD (Fig. 1). The results are in agreement with kinetic studies that show E binds the protonated form of L-Phe more tightly than EH, thus in effect decreasing the value of pK_{EH} .

Addition of azide to ZnCPD-L-Phe at pH 7 markedly changes the Zn coordination sphere (Fig. 2) from 4 N/O atoms at 2.021 Å and 1.4 N/O atoms at 2.54 Å to 3.9 N/O atoms at 1.995 Å. The XAFS spectra of the ternary complex is pH independent from 7 to 9 (Fig. 2) in agreement with the ionization of the water being the source of the spectral changes in the free enzyme and its binary L-Phe complex (2). The enzyme-azide-L-Phe complex is likely bound in a manner analogous to that expected for a post-transition state in a bi-product complex for peptide hydrolysis i.e. the carboxylate anion of the peptide bound to the Zn and the protonated form of L-Phe H-bonded to the catalytic Glu-270 carboxylate.

1. Zhang, K. & Auld, D. S. Biochemistry 32, 13844-13851, 1993.

2. Zhang, K. & Auld, D. S. Biochemistry, in press.

Figure 1. XAFS spectra of ZnCPD-L-Phe at pH 6.56 (solid) and 8.83 (circles).

Figure 2. RDF of ZnCPD-L-Phe-azide at pH 7.0 (solid) and 8.81 (circles) and ZnCPD-L-Phe at pH 6.65 (diamonds).

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Phase Behavior of Liquid Crystals in Silica Aerogels *

X10A

Noel A. Clark, A.G. Rappaport, T. Bellini, and B.N. Thomas (University of Colorado, Department of Physics, Condensed Matter Laboratory, Boulder, CO)

Phase behavior in the presence of externally induced disorder is an area of current research in statistical physics. Liquid crystals (LCs) are particularly interesting in this context. Because they possess rather weak orientational and partial translational ordering, which is readily affected by surface interactions, the phase behavior of liquid crystals can be strongly influenced by incorporation into porous solid media of high surface to volume ratio. The most basic LC translational ordering is the nematic - smectic A (NA) transition, wherein a one dimensional layering of molecules into a stack of 2d liquid-like layers appears.

We report the results of an X-ray diffraction study of the smectic A layer structure with the liquid crystal incorporated into the pores of silica aerogel. This is the first quantitative study of the effect of externally induced disorder on liquid crystal layer structure. The LC is incorporated into silica aerogels, highly porous solids formed by dehydration of suspensions of aggregates of nm dimension silica particles. The aerogel pores, ranging in mean size from 120 Å to 700 Å form a continuously connected volume which can occupy a volume fraction ϕ approaching unity ($\phi \leq 0.95$ in the experiments reported here), of high surface to volume ratio. The results show that the aerogel confinement radically alters the nematic - smectic A transition. At the lowest temperatures local smectic ordering extends out to dimensions comparable to the pore size or somewhat larger, but for temperatures near the bulk nematic - smectic A transition, the smectic order is strongly suppressed.

Figure 1. Correlation lengths for smectic A ordering vs temperature T for bulk 8CB and 8CB in a series of silica aerogels of indicated pore size. The divergence at the bulk NA transition of the bulk correlation lengths for smectic ordering along the director ($\parallel$) and normal to the director ($\perp$) is also shown. The smectic order is strongly suppressed at temperatures near the bulk transition, but ultimately grow to be comparable to or larger than the pore size. Although the bulk smectic correlations are highly anisotropic [$\xi_{\parallel} \gg \xi_{\perp}$], the x-ray lineshapes show that in the aerogel the correlations are nearly isotropic.

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Chain Length Dependence of the $C_n/Au(111)$ Tilt Structure *

X10A

P. Fenter, A. Eberhardt, K. S. Liang and P. Eisenberger (Princeton Univ.)

We use grazing incidence x-ray diffraction to study the systematic structural dependence of an archetypal self-assembled monolayer as a function of the chain length, n . The monolayer consists of n -alkyl thiol molecules, $CH_3(CH_2)_{n-1}SH$ (C_n , $10 \leq n \leq 30$), self-assembled on a $Au(111)$ surface. At room temperature, the 2D structure is described by a $C(4 \times 2)$ unit mesh [1,2,3] at all chain lengths. We find that there is a systematic dependence of the tilt structure as a function of the hydrocarbon chain length which is characterized by distinct 'long' ($n \geq 16$) and 'short' ($n \leq 14$) chain length regimes, as well as a continuous structural variation within each regime [4]. For example, the tilt angle for $n \leq 14$ is 3° greater than the tilt angle for $n \geq 16$, and the tilt direction shows a clear trend of shifting away from the NNN direction as the chain length decreases. Furthermore, there appears to be a discontinuous change in the tilt angle between these two regimes. A parameterization of the hydrocarbon packing leads to the conclusion that the long and short chain length regimes closely resemble the orthorhombic and monoclinic chain packing of n -alkanes. These systematic structural changes are apparently due to the conflicting requirements of epitaxy and molecular packing, and is driven by the changing intra-layer interaction

strength (which is proportional to hydrocarbon chain length).

[1] N. Camillone III, C. E. D. Chidsey, G.-Y. Liu, and G. Scoles, J. Chem. Phys. 98, 3503 (1993).

[2] P. Fenter, P. Eisenberger, and K. S. Liang, Phys. Rev. Lett. 70, 2447 (1993).

[3] P. Fenter, A. Eberhardt, and P. Eisenberger, Science 266, 1216 (1994).

[4] P. Fenter, A. Eberhardt, K. S. Liang and P. Eisenberger, submitted (1995).

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Growth of Self-Assembled Monolayers: Decanethiol/Au(111)

X10B

A. Eberhardt, P. Fenter, B.T.Y. Leung, and P. Eisenberger (Princeton U.)

The adsorption kinetics of decanethiol ($\text{CH}_3(\text{CH}_2)_9\text{SH}$) self-assembled on Au(111) have been investigated by grazing incidence x-ray diffraction. The monolayers were formed on a clean single-crystal gold substrate by vapor deposition in a small UHV chamber. The diffraction intensities were measured both in real time and in an interrupted growth mode, to examine partial layers more carefully. The growth curves are consistent with Langmuir kinetics, in which the adsorption rate is proportional to the number of remaining sites. The initial sticking coefficient has been found to be on the order of 10^{-5} at room temperature. A preliminary phase diagram as a function of temperature and coverage has been developed, including at least three different phases: the close-packed C(4X2) unit cell, a striped phase, and a disordered, melted phase.

Two different adsorption mechanisms have been found; one dominates at higher temperature ($> 30^\circ\text{C}$), the other at lower temperature ($< 5^\circ\text{C}$). These are believed to correspond to direct and to physisorption-mediated chemisorption, respectively. At low temperature, the growth rate increases as the square of the thiol pressure, implying a bimolecular transition from the physisorbed to the chemisorbed state. This could be explained if the surface structure is composed of disulfides [1], or if a molecular hydrogen is required in the reaction products to make the process energetically favorable. The low temperature growth rate decreases exponentially with increasing temperature, strongly suggesting a physisorbed precursor, with an activation energy of about 1.4eV. In contrast, the high temperature rate is independent of temperature over the range studied (-15°C to 70°C), and increases linearly with increasing pressure. The observations are consistent with a combination of a simple, direct chemisorption reaction, and a more complicated two-molecule adsorption process involving an intrinsic physisorbed precursor state.

[1] P. Fenter, A. Eberhardt, and P. Eisenberger, Science 266, 1216 (1994).

Structure and Evolution in an Organic Thin Film: PTCDA/Au(111)

X10B

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P. Fenter, L. Zhou, P. E. Burrows, S. R. Forrest and P. Eisenberger (Princeton Univ)

We have used grazing incidence x-ray diffraction to study the growth of 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA) on Au(111) under ultra-high vacuum by organic molecular beam deposition. PTCDA is an archetype planar crystalline organic molecule, which we are using to study the fundamental

We find that the film morphology and strain depend strongly upon the growth conditions (i.e., growth rate and substrate temperature). While "flat" films (having, for instance, a few monolayer roughness for a 17ML film) can be grown at low substrate temperature and fast growth rates, a 3D morphology is observed (with a thin wetting layer) under more equilibrium conditions (slow growth and high substrate temperatures). These observations suggest that PTCDA incompletely wets Au(111) at equilibrium, but that kinetic barriers are sufficiently high to stabilize the "flat" films grown under non-equilibrium conditions.

Our initial measurement of the film structure and order [1] demonstrated that these PTCDA films are highly ordered, and exhibit a well defined film thickness. The films are orientationally aligned to the Au substrate within the surface plane (with an in-plane mosaic of $1-2^\circ$). We also have determined that the film is strained, which is characterized as a change in the a/b ratio of the 2D unit mesh.

We have begun to extend these studies to determine the evolution of strain as a function of film thickness. We have found that under the non-equilibrium conditions in which PTCDA grows in a "flat" film morphology, the film exhibits both a significant strain of 8%, which is independent of the film thickness to at least 70ML (200Å). The film also exhibits an inhomogeneity along the alignment direction, which decreases linearly to zero over this range of film thicknesses. This clearly shows that a significant strain can be "locked-in" to the lattice of molecular lattices under kinetically limited growth conditions.

[1] P. Fenter, P. Burrows, P. Eisenberger, and S. R. Forrest, J. Cryst. Growth 152, 65 (1995).

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Structure of ω -Substituted Self-Assembled Monolayers *

X10B

T. Y. B. Leung, A. Eberhardt, P. Fenter, P. Eisenberger, and G. Scoles (Princeton Univ)

We have performed initial grazing incidence x-ray diffraction studies of the structure of ω -substituted alkyl thiols, $\text{CH}_2=\text{CH}-(\text{CH}_2)_9-\text{SH}$, self-assembled on Au(111) surfaces to determine what affect small chemical changes may have upon the monolayer structure and properties, and as a clear structural basis for understanding the stereochemistry of reactive beams with the terminal double bond. The monolayers are grown by vapor deposition, and studied under ultra-high vacuum conditions.

Although the substitution of the inert $-\text{CH}_3$ group by a double bond functionality was not expected to have a significant impact upon the monolayer structure, our initial results indicate that these monolayers have a 2D structure different from that of the $-\text{CH}_3$ terminated compounds, and remarkably, exhibit a much higher thermal stability. The unit mesh of the ω -substituted monolayer has dimensions of $4.997\text{\AA}$ by $17.32\text{\AA}$, as compared to the $\text{C}(4\times 2)$ structure [1,2] of the $-\text{CH}_3$ terminated monolayer which has dimensions of $9.994\text{\AA}$ by $8.66\text{\AA}$. Furthermore, the ω -substituted monolayer does not exhibit the centered rectangular symmetry found for the $-\text{CH}_3$ terminated monolayer [3], since we do not find any systematic absences of the Bragg rods.

A second surprising feature is that the thermal stability of this system is much higher than that of the alkyl thiol system. For instance, we find that the ω -substituted monolayers begin to show signs of re-arrangement at temperatures above 120°C , whereas similar chain length alkyl thiols melt at approximately 65°C . These observations indicate that small changes to the molecular structure can induce large changes in the monolayer structure and stability.

[1]N. Camillone III, C. E. D. Chidsey, G.-Y. Liu, and G. Scoles, J. Chem. Phys. 98, 3503 (1993).

[2]P. Fenter, P. Eisenberger, and K. S. Liang, Phys. Rev. Lett. 70, 2447 (1993).

[3]P. Fenter, A. Eberhardt, and P. Eisenberger, Science 266, 1216 (1994)

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Fe and Mo K -edge EXAFS of CO-inhibited *A.v.* Nitrogenase

X10C

B. J. R. Weiss, S. P. Cramer (U. C. Davis), R. Tittsworth, and B. J. Hales (Louisiana State U.)

Nitrogenase is nature's agent for fixing nitrogen, converting atmospheric dinitrogen into ammonia for plant, animal and human consumption. The enzyme contains two metalloproteins: the Fe protein, which contains an Fe:S center, and the larger MoFe protein, containing both an Fe:S cluster and the Mo:Fe:S cofactor. While the crystallographic structure of the resting state is known, CO and (of even greater interest) N_2 bind to reduced states which cannot be crystallized, and whose structure is unknown.

We are using both Fe and Mo K -edge EXAFS to look for structural changes in the reduced intermediates and to determine which atoms are involved in substrate and inhibitor binding. While there are multiple iron atoms in each of the proteins, there is a single molybdenum atom located at the active site; thus, information from the Mo K -edge is much more specific, and any shifts should be indicative of a change in the redox state of molybdenum, and imply direct involvement of the Mo atom in nitrogen fixation.

EXAFS scans were taken at both the Fe and Mo K -edges of CO-inhibited *A.v.* nitrogenase. We were able to reproduce previous data sets, and the resulting fourier transforms are shown below compared to Fe and Mo EXAFS of resting state *A.v.* nitrogenase. Further analysis is currently underway.

Preliminary work was also done on C_2H_2 -inhibited *A.v.* nitrogenase at both Fe and Mo K -edges, and on "deep turnover" nitrogenase at the Mo K -edge.

Figure 1. Fourier transforms of Fe K -edge EXAFS

Figure 2. Fourier transforms of Mo K -edge EXAFS

Lead Speciation of a Mixed Soil Component System Using EXAFS X11A

T.E. Alcacio, G.M. Lamble*, A. Scheidegger and D.L. Sparks U. of Delaware, *NSLS, BNL

The chemical behavior of any element in the environment depends on the nature of its components. Most natural systems are quite heterogeneous and have both mineral and organic phases present. Thus, there is a potential for many species to be present. The actual form or species needs to be determined in order to gain insight into the physical chemistry of natural systems as well as into the nature of pollutant interactions. In this study, Extended X-ray Absorption Fine Structure Spectroscopy was utilized to determine the local chemical environment of Pb treated pyrophyllite and gibbsite. Both minerals were then mixed together in a 1:1 ratio and studies of the EXAFS spectra was performed as well. The radial distribution function for the gibbsite shows a first coordination shell occurring at 2.01 and a second coordination shell at 3.60 . These distances, which are uncorrected for phase shifts, are comparable to bond distances expected for Pb-O and Pb-Pb respectively. In contrast, the pyrophyllite which has nearly a 4X greater surface area shows only one peak at 1.90 (Pb-O) and no second coordination shell.

We suggest the formation of Pb polynuclear species on the gibbsite surface results from greater crowding of lead atoms on the surface.

When the two samples undergo mixing, the spectra for the mixed component system agrees well with the prominent features displayed by the spectra for the two individual components. It is hoped that this study will spur further investigations of heterogeneous systems which model natural systems.

Figure 1. Fourier transform of pyrophyllite (lower), gibbsite (middle), and mixture(top) of both.

Chromium speciation in hazardous, cement-based waste forms X11A

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Chromium contaminated waste streams can result from metal plating or finishing processes, where Cr is usually present as the highly soluble and toxic CrO_4^{2-} species. Cement-based forms are frequently used to immobilize such liquid wastes. Studies on chromium release from these waste forms indicate that CrO_4^{2-} diffuses rapidly, and is significantly more mobile than reduced Cr^{3+} . Consequently, formulations of cements have been developed to control the chromium speciation in situ to favor the less soluble and less mobile Cr^{3+} ion. Therefore the knowledge of the oxidation state and local environment of Cr in situ is essential to predict long-term contaminant release from the waste form.

XANES and EXAFS techniques were used to determine the oxidation states and local environment of Cr in cement-based waste forms. Simulated waste solutions were prepared using Na_2CrO_4 , and mixed with cement materials to give 2500 ppm Cr in solid matrix. Three mixtures and two standards were analyzed in this experiment (Table 1). Mix 1 consisted of slag, Mix 2 of slag, fly ash and Portland cement, and Mix 3 of Portland cement only. Figure 1 shows the near edge spectra from the Cr K-edge of five samples. It is quite clear that the structural environment of Cr in Mix 1 is very similar to Cr in CrOOH . The XAFS spectrum Cr in Mix 3 and Mix 1 agree very well with those of Cr-O in CrO_4^{2-} and CrOOH , respectively. The large difference in the Cr-O distances in these two environments are easily distinguishable. Coordination numbers for Mix 2 suggest that this mixture consists of about 25% Cr^{6+} and 75% Cr^{3+} species (Table 1).

Results show that the Cr in untreated Portland cement formulations remains as toxic Cr^{6+} , while slag additives to the cement reduce Cr^{6+} to the less toxic, less mobile Cr^{3+} species. EXAFS analysis suggests that the Cr^{6+} species is surrounded by four nearest oxygen neighbours, while reduced Cr^{3+} species is surrounded by six oxygen atoms.

Figure 1. Near edge spectra from Cr K-edge of K_2CrO_4 (a), Mix #3 (b), Mix #2 (c), Mix #1 (d) and CrOOH (e).

Table 1

Sample	N (±25%)	R(±0.02) in Å
K_2CrO_4	4.90	1.65
mix #3	5.40	1.66
mix #2	1.31, 4.93	1.65, 1.98
mix #1	6.46	1.98
CrOOH	6.21	1.98

Figure 2. (Table)

XAFS and Developing Plants for Phytoremediation

X11A

W.R. Berti (Du Pont), G.M. Lamble (BNL), S.D. Cuninghame, and J.W. Huang (Du Pont)

Traditional solutions to remediate Pb-contaminated soils rely primarily on excavation, stabilization with cement, and landfilling. These techniques are invasive and expensive, resulting in drastically disturbed soils and landscapes. Phytoremediation uses plants and soil conditioning agents to remediate contaminated soils in an "eco-friendly" manner.

Phytoextraction, or biomining, uses plants to remove or destroy contaminants from the soil matrix. For the phytoextraction of Pb, there is a need to find, breed, or develop plants that can translocate Pb from roots to the tops. The Pb is then removed by harvesting and processing the above ground portion of the plants. For this technology to be effective, however, plant tops must "hyperaccumulate" Pb in excess of 1% (dry-weight basis). We regularly find roots of plants that contain as high as 1%. The tops of these plants, however, rarely have total Pb concentrations as high as 0.1%. Information provided by XAFS about the forms of Pb in plant parts and its location within the plant may be valuable in this research. It may help guide selection of plant species and traits to use in the development or breeding of Pb-hyperaccumulating plants.

The figure shows overlaid XAFS data from Pb uptaken in corn roots and in ragweed. Well defined features in the spectra indicate that the Pb structural form is also well defined. The similarities between the spectra indicate that the Pb is uptaken in a very similar form in both the ragweed and the corn roots.

Figure 1. Comparison of raw XAFS data from Pb uptaken by Corn Roots (solid line) and Ragweed (broken line).

Progress in fabricating capillary fibers for x-ray concentrators

X11A

D.L. Brewster (U. of Washington), S.M. Heald (Pacific Northwest National Lab), B. Barg, F.C. Brown, K.H. Kim, and E.A. Stern (U. of Washington)

Guiding x-rays down the inside of tapered capillaries is a means to increase the flux density from synchrotron light sources, without some of the disadvantages inherent in some other techniques. We have demonstrated that a process based on techniques for fabrication of glass fibers may be used to produce tapered capillaries with inlet diameters on the order of 150 μm or more and outlets on the order of 1 μm or less¹. Several capillaries made from pure silica glass were manufactured and the performance was tested at X11A. Pure silica has the advantages of radiation hardness, and freedom from potential problems arising from fluorescence of heavier elements in the capillary, in formulations such as lead glass. Measured transmission of x-rays from linear capillaries with inlet diameters of $\sim 150 \mu\text{m}$ and outlet diameters of 1.3 – 1.4 μm is on the order of 2% for an x-ray energy of 10 KeV, with corresponding intensity gains of up to ~ 270 (see Table).

Calculated and measured transmission efficiencies are in fairly good agreement, leading to the expectation that efficiencies predicted by calculations to be attainable from optimal profiles² are a realistic goal. We have also made progress in fabricating capillaries with profiles predicted by calculations to provide greatly improved transmission over the linear capillaries. We are in the process of testing these capillaries, and constructing improved apparatus for supporting and aligning the capillaries in the x-ray beam.

[1] K.F. Voss, K.H. Kim, E.A. Stern, F.C. Brown, and S.M. Heald, Nucl. Inst. Meth. A347, 390 (1994).

[2] D.L. Brewster, S.M. Heald, B. Barg, F.C. Brown, K.H. Kim, and E.A. Stern, SPIE Proc., Vol. 2516 (1995).

capillary	length	inlet/outlet diameters	intensity gain	measured efficiency	calculated efficiency
#17	875mm	106/12.4 μm	32	44%	99.5%
#19	548mm	150/1.3 μm	274	2.1%	4.25%
#12	360mm	145/1.4 μm	239	2.2%	2.90%

Figure 1. Summary of measurements and calculations for three capillaries. The x-ray energy for the measurements was 10 KeV.

Yuan Dao, Robert J. Nemanich, and Dale E. Sayers (North Carolina State University)

Previously, we have been shown that the C49 phase of TiSi_2 can be stabilized at high temperatures by co-evaporation of a small amount of Zr with Ti. The resulting C49 Ti-Zr alloy silicide thin films exhibit improved thermal stability compared to C54 TiSi_2 films. In order to understand this further, the local atomic structure around the Ti and Zr sites was studied using extended x-ray absorption fine structure (EXAFS) analysis (See Fig. 1). The distances of the Ti-Si and Zr-Si shells in the C49 $(\text{Ti}_{1-x}\text{Zr}_x)\text{Si}_2$ thin films are similar to those of the Ti-Si and Zr-Si shells in the C49 TiSi_2 and ZrSi_2 respectively, and do not change with composition. This is a Bragg-Pauling like behavior. The Ti-Ti distances in the C49 $(\text{Ti}_{1-x}\text{Zr}_x)\text{Si}_2$ thin films vary linearly with the Zr content x . The Ti-Zr shell distance in the C49 alloy silicide thin films is longer than the Ti-Ti distances. The Ti-Ti shell in the C49 alloy silicide thin film splits into two sub-shells.

The Ti-Ti short distance increases more significantly with the Zr content than that of the Ti-Ti long distance. The Ti-Ti short distance shell in the C49 alloy silicide is more disordered than that of the Ti-Ti long distance. This may be due to the asymmetry of the Ti-Ti short distance shell, and therefore, the Ti-Ti short distance shell may have the ability to adjust its lattice positions to lower the strain energy introduced by the Zr atoms. The C54 TiSi_2 has only one Ti-Ti shell, which is symmetric about the central Ti atom and may not have the ability to adjust the lattice positions to lower the strain energy.

Figure 1. Fourier transforms (solid lines) and the R-space fitting results (dotted lines) of k^3 -weighted Ti K-edge EXAFS of the C49 $(\text{Ti}_{1-x}\text{Zr}_x)\text{Si}_2$ thin film samples ($x = 0, 0.1, 0.2$ and 0.3).

Monica Endregard (Univ. of Trondheim, Norway), and Alex F. Gualtieri (Univ. of Modena, Italy)

Kaolinite is the main mineralogical component in clays. Besides, its importance resides in the large use of this mineral as a precursor for ceramic products. Its structure consists of a stacking of 1:1 Si centered tetrahedral and Al centered octahedral layers along the c axis. The way the layers stack can be affected by extensive faulting (planar disorder) resulting in low-defective and highly-defective structures such as kaolinite international standards KGa-1 and KGa-2 which contain 14 and 50 % of faulted sequences, respectively. The structural state of kaolinite influences the kinetic of the HT processes leading to the formation of metakaolinite and mulite.[1] Because abrupt transformations affect the octahedral Al environment of the faulted sequences during the phase transitions, a study of such changes may provide information about the process. Mössbauer [2] and EPS [3] studies showed that Fe in natural kaolinites usually substitutes for Al in the lattice. Thus, an XAFS study of Fe bearing kaolinites thermally treated at various temperatures can be highly informative concerning these structural changes. Fe K-edge (7112 eV) XAFS spectra of KGa-1 and KGa-2 at RT, 600, 800 and 1100 °C and selected model compounds were collected simultaneously in transmission and fluorescence mode at 298 and 80 K. The energy calibration was checked by simultaneously measuring XAFS on a Fe foil using a reference detector. The higher harmonic reflections were rejected by detuning the Si(111)monochromator crystals to 70 %. The information contained in the XANES spectra coupled with the EXAFS analysis suggests that the Fe coordination decreases upon thermal treatment from 6 to 4 accompanied by a shortening of first shell bond distances.

- [1] Gualtieri A.F. (1995). PhD thesis, Univ. of Modena, Italy.
- [2] MacKenzie K.J.D. (1969). Clay minerals 8, 151-160.
- [3] Jefferson D.A., Tricker M.J., and Winterbottom A.P. (1975). Clays and Clay Min. 23, 355-360.

Figure 1. Fourier transform magnitude of the k^3 weighted Fe K-edge EXAFS of disordered kaolinite samples (KGa-2) at RT and heated at 600°C and 800°C.

* This work was supported by The Norwegian Research Council and DOE under contract numbers DE-AC02-76CH00016 and DE-FG05-89ER45384.

XAS Studies of Highly Nonplanar Cobalt(III) Porphyrin Complexes *	X11A
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Elucidating the coordination geometries of metalloporphyrins is a crucial aspect of understanding the biological activity of these systems. Where diffraction quality crystals are available the method of choice is single crystal x-ray crystallography, although for microcrystalline materials and solutions other methods such as XAS have proved to be valuable [1- 3]. Recently, the Davis group has synthesised a number of extremely nonplanar Co(III) porphyrins with novel ligand orientation properties [4], a topic currently of interest because of the role different ligand orientations might play in modulating the redox potentials of cytochromes [5]. Since the nonplanar cobalt(III) complexes do not yield crystals suitable for x-ray structure determinations we are seeking information about the ligand binding geometries from XAS studies. An important question in these systems is whether the unusual ligand orientation (ligand plane over N atoms) causes an elongation of the axial Co-N distance. The macrocycle can also adopt a severely distorted conformation in order to minimise the steric strain between the peripheral substituents. Information about the conformation of the macrocycle may be obtained by XAS since it is correlated to the metal to nitrogen bond distance. This study also includes investigations on the state of these complexes in solution, an aspect of particular importance for the biological role of these compounds. We have collected transmission XAS data on octaethyltetraphenylporphyrinato cobalt(III)chloride (OETPP-CoCl) complexed with pyridine and tetratertbutyl-porphyrinatocobalt(III) chloride (TtBuPCoCl) complexed with pyridine and 1-methylimidazole, respectively. In 1996, we hope to collect data on the remaining nonplanar cobalt(III) porphyrin complexes in solution required for completion of our studies.

[1] Furenlid, L. R., Renner, M. W., Smith, K. M. and Fajer, J., J. Am. Chem. Soc. 112 (1990) 1634, 8987.

[2] M. Endregard, D. G. Nicholson, R. J. Abraham, I. Marsden and B. Beagley, J. Chem. Soc., Faraday Trans. 90(18) (1994) 2775.

[3] M. Endregard, D. G. Nicholson, R. J. Abraham, I. Marsden and B. Beagley, Acta Chem. Scand. 48 (1994) 640.

[4] Medforth, C. J., Muzzi, C. M., Smith, K. M., Abraham, R. J., Hobbs, J. D. and Shelnutt, J. A., J. Chem. Soc., Chem. Commun., 1994,1843.

[5] Safo, M.K., Walker, F.A., Raitsimring, A.M., Walters, W.P., Dolata, D.P., Debrunner, P.G., Scheidt, W.R., Osvath, S.R., J. Am. Chem. Soc., 1994, 116, 7760.

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CVD Growth of III-V Quantum Wires and Dots in Microporous Hosts; Indium K-edge XAFS of the Local Coordination of the III-V Semiconductor Clusters *	X11A
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Wendy Flavell, Heather Yates and Jonathan Agger (UMIST, UK), David Nicholson and Arild Moens (Univ. of Trondheim, Norway), Geraldine Lambie and Larry Fareria (BNL)

This work is aimed at the growth of ordered quantum wire and dot structures inside the cage and channel structure of host microporous materials, by deposition of compound semiconductors. Here, we aim to use XAFS to study the local environment of InP clusters introduced into materials including $\text{AlPO}_4\text{-5}$ and MCM-41 by MOCVD. The work forms part of an EC ESPRIT III Basic Research Project.

The reactants used in the MOCVD growth were trimethylindium and phosphine in hydrogen carrier gas, and these were introduced sequentially into the host material. Station X11A was used to study the In K-edge of the implanted semiconductor. These measurements were complemented by studies of the P K-edge using station 3.4 at SRS, CLRC Daresbury Laboratory, UK, and by ^{31}P MASNMR, EDAX, XRD, HRTEM and PL.

Analysis of the In K-edge data from $\text{AlPO}_4\text{-5}$ samples loaded with differing amounts of InP showed that long range order is maintained within the implant.

The position of the first P shell in all samples was unchanged from its distance of 2.54 Å in a bulk InP standard. The first In shell was located at 4.17 Å, very close to its distance in InP. Additional oxygen atoms at around 3.45 Å were located, originating from the bonding of the implant to the zeolite framework. These observations confirm suggestions from MASNMR, PL and from P K-edge EXAFS that the local structure of the implant is not significantly distorted from that in bulk InP. This result is in contrast to measurements taken from a sample in which only the first of the MOCVD reagents, trimethylindium, was introduced into the host. Here, strong bonding of In to the zeolite framework was observed, with 3 O atoms coordinated at 2.14 Å. No long range order which could be attributed to bulk In was observed. This confirms earlier work by ^1H NMR and CARS, which suggested that the first introduced MOCVD precursor reacts at the acid sites within the zeolite [1].

[1] M.W. Anderson, G.K. Logothetis, M.E. Pemble, A.G. Taylor, N.C. Wallace and H.M. Yates, J. Adv. Mater. Opt. Elect. 2, 313(1993).

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Solution of the structure of disordered mixed salts

X11A

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We have solved, for the first time, the structure of a disordered system of mixed salts including its buckling about the average structure, using X-ray absorption fine structure (XAFS) method and molecular dynamics (MD) simulations. Recent XAFS measurements on mixed disordered crystals of the average NaCl structure have revealed essential differences from the periodic structure [1]. We have extended the measurements to span the full range of concentrations in the $\text{RbBr}(x)\text{Cl}(1-x)$ system. We find that the concentration - weighted average of interatomic distances determined with XAFS is greater than the interplanar spacing, given by diffraction, the gap between the two being as large as 0.04(1) in the middle of the x-range. Such a difference is consistent with bond buckling [1]. We determined the buckling angles by XAFS analysis and rms values of the buckling angles were found to maximize at 10-12 deg. for the 50 % concentration of Br at 10 K. We demonstrate also that the buckling has to be accompanied by lattice strains and obtain the strain energy from the MD simulations. Simulations have shown that the strains are necessary to maintain the average NaCl structure of these systems. We estimate that the strain energy, measured at low temperature, would be partially (55 %) released at the elevated temperatures, due to the thermal expansion. The residual strain energy was used to estimate the melting point depression of these mixtures and excellent agreement with experiment is found.

1. A. Frenkel, E. A. Stern, A. Voronel, M. Qian, M. Newville, Phys. Rev. Lett., 71, 3485 (1993); Phys. Rev. B 48, 12449 (1993).

Nature of the Sr induced structural phase transition in

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

X11A

D.Haskel and E.A.Stern (University of Washington)

The local structure about La atoms in oriented $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ crystals is investigated by means of polarized X-ray Absorption Fine Structure (XAFS) measurements. Diffraction results [1] indicate that the Sr induced structural transformation at low temperature from orthorhombic (LTO) to tetragonal (HTT) involves decreases, on the average, of the tilt angle of the CuO_6 octahedra to zero (Fig. 1). Magnetic measurements [1] show that bulk superconductivity persists in the HTT phase, with no apparent effect of the structural phase boundary on the transport properties.

Polarized XAFS results [2] show that the Sr induced phase transition exhibits displacive character, at least up to $x \approx 0.15$, which is manifested through a decrease in the tilt angle of the CuO_6 octahedra, in agreement with the diffraction results. At higher Sr content, however, the local tilts stop changing but start disordering over long range giving raise to the average HTT structure (Fig. 2). The absence of an effect of the Sr induced phase boundary at low-T on the superconducting properties is probably related to the lack of a significant change in the local structure over scales comparable to the superconducting coherence length in this material. This suggests that the correlation length of LTO tilts in the superconducting HTT phase is somewhat greater than $30\text{\AA}$, a result that can be confirmed by other techniques sensitive to intermediate range order such as the Pair Distribution Function (PDF) of neutron diffraction or atomic resolution imaging in the TEM.

We acknowledge the valuable help of F. Perez, M. Suenaga and S. Heald in orienting the samples. This research has been supported by D.O.E. grant #DE-FG06-90ER45425.

[1] P. G. Radaelli *et al.*, Phys. Rev. B 49, 4163 (1994)

[2] D. Haskel *et al.*, Phys. Rev. Lett. 76, p.439 (1996).

Figure 1. Schematic representation of the LTO structure. In the HTT phase, diffraction results indicate that the tilt angle of the CuO_6 octahedra is, on the average, zero.

Figure 2. La-O(2) distances as a function of x as obtained from the polarized XAFS analysis at T=20K. The neutron diffraction results are also shown.

XAFS Studies of MnSe/ZnTe Superlattices

X11A,
X23A2

A. J. Kropf, B. A. Bunker, J. K. Furdyna, Q. Lu (Notre Dame), and K. M. Kemner (NRL)

Polarization dependent XAFS, employing the total electron yield (TEY) and energy discriminating fluorescence detection techniques, has been used to study the structure of MnSe/ZnTe (001) superlattices grown by MBE. These superlattices consist of 100-300 periods of A/B layers with A and B ranging between 4 and 25 monolayers. Neutron scattering data on these materials show an unique anti-ferromagnetic helimagnetic phase at low temperature which is tunable by varying the thickness, temperature and strain of the MnSe layer (T. M. Giebultowicz, et. al., Phys. Rev. B (Rapid Comm.) 46, 12076, 1992).

Of particular interest is the interface between the magnetic MnSe layers and the ZnTe layers, which act as a non-magnetic buffer, magnetically isolating the individual MnSe layers, and the effect of the interface on the strain in the MnSe layers. Polarization dependent XAFS taken at different edge energies coupled with x-ray diffraction results can distinguish between different models of the structure at the interface.

In the data shown below, one can clearly see the effect of the lattice mismatch between MnSe and ZnTe as the MnSe bonds bend, while stretching only minimally, to accommodate the ZnTe lattice spacing. This reduces the first shell amplitude of the the XAFS for x-ray polarization vector perpendicular to the plane of superlattice growth relative to the amplitude of the XAFS for the polarization vector in the plane of the superlattice layers.

Figure 1. Mn Edge Fluorescence Data (Sample 900622A)

EXAFS Studies on Cu(II) Ions Exchanged in H-SAPO-5 and CoSAPO-5 and -34 Molecular Sieves

X11A

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Microporous, microcrystalline aluminium phosphates (ALPOs), metal-substituted aluminium phosphates (MeALPOs) and silicon-substituted analogues (SAPOs) are interesting candidates for catalytic studies and there is a continuing growth in the size of the family of compounds since they were first synthesised in 1982[1].

Because of their structural relationships to the zeolites the materials are often termed zeotypes. The zeotypes are monophasic crystalline solids in which the active sites are distributed in a spatially uniform manner throughout the bulk. Thus, some of them can be used as uniform heterogeneous catalysts. In this connection, the most significant feature of zeotypes is their microporous nature which means that nearly all of the accessible surface area is actually inside the crystallites. For example, over 99.5% area of a 1mm diameter crystallite is internal. Consequently, most of the Al, P and/or metal atoms are effectively surface atoms, although they are located deep inside the material and this means that bulk physical techniques such as EXAFS can actually be regarded as surface techniques in these special cases. We have previously published some results of EXAFS studies using the facilities of X11A [2 - 4]. In CoSAPO-34 the cobalt atoms enter the framework by substituting Al(III) in the form of Co(II). The material is interesting because it undergoes colour changes on calcination (blue to green at 500 C with a change to greyish-blue on cooling in moist air). The object of the present study is use XAS to study the environments of the Cu- and Co- atoms in the as-synthesised and calcined materials. EXAFS and other techniques show that attempts to incorporate Cu into the framework of the molecular sieve during the hydrothermal synthesis lead to reduction to Cu(I) with subsequent disproportionation to Cu-metal [5]. Data were collected for a series of formulations a liquid N2 temperature. The results of this first part of the XAS study are currently being analysed. We have recently measured the catalytic activity with respect to NO reduction [6] and the next stage in the study is to record XAS of selected samples in an in situ cell.

[1] S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannan, E.M. Flanigen, J. Am. Chem. Soc. 1982, 104, 1146

[2] A. Lund, D.G. Nicholson, G. Lamble and B. Beagley J. Materials Chem., 1994, 4, 1723.

[3] M. Endregard, D.G. Nicholson, M. Stcker and G. Lamble J. Materials Chem., 1995, 5, 485.

[4] M. Endregard, D.G. Nicholson, M. Stcker and G. Lamble J. Materials Chem., 1995, 5, 785.

[5] A. Moen and D. G. Nicholson, J. Chem. Soc. Faraday Transactions, 1995, (in press)

[6] A. Moen, Ph.D Thesis, Trondheim, 1995.

XAFS study of Zn^{2+} incorporation into calcite (CaCO_3)

X11A

Geraldine M. Lambie (BNL) and Richard J. Reeder (SUNY, Stony Brook)

The mobility and abundance of Zn^{2+} and other heavy metal species in natural waters are largely controlled by uptake onto mineral surfaces via adsorption or coprecipitation. Coprecipitation of dissolved heavy metal species with calcite, CaCO_3 , is known to be very effective in limiting dissolved concentrations and restricting mobility. However, recent coprecipitation studies have documented that dissolved metal ions show distinct preferences for different surface sites during layer growth. Zn^{2+} shows a surface site preference that differs from the behavior expected on the basis of ion size. Although differential incorporation occurs at distinct surface sites, it has been thought that Zn^{2+} occupies only the single Ca site in the bulk.

As a first step toward understanding the Zn^{2+} incorporation mechanism, we have obtained XAFS spectra of the Zn K-edge (9659 eV) for synthetic Zn-bearing calcite samples. The fitting results for the Zn-bearing calcite indicate a Zn first shell with 6.7 (+/- 1.0) oxygen atoms at a distance of 2.11 (+/- 0.02) Å. These values compare favorably with expected values for Zn in octahedral coordination with oxygen. This suggests that Zn^{2+} occupies only the Ca site in the bulk structure. Therefore, the different surface sites represent multiple surface expressions of a single bulk site.

Figure 1. Fourier transforms of raw XAFS data from the K-edge of Zn in Calcite (full line) with that of Zn in ZnCO_3 (broken line). The coincidence of the first Fourier transform peak provides a direct indication that Zn is in an octahedral coordination with O, as in ZnCO_3 and thus occupies the Ca site in calcite, as is confirmed by the XAFS analysis.

XAFS Investigation of Thermal Structural Disorder at GaSb/AlSb Superlattice Interfaces

X11A,
X23A2

Q. Lu, B. A. Bunker, A. J. Kropf, S. W. Short, S. H. Xin, J. K. Furdyna (Notre Dame)

Although surface melting is now well established, the comparable effect at internal interfaces has not been studied to anywhere near the same extent. As part of a larger program to study interfacial properties, we have studied GaSb/AlSb superlattices using X-ray Absorption Fine Structure (XAFS) with total electron yield (TEY) detection. These Ga K-edge measurements have focussed on thermal vibration amplitudes as a function of temperature, polarization, and GaSb layer thickness (either 20 Å or 40 Å). In XAFS measurements, the thermal vibration amplitude is reflected in the relative radial Debye-Waller (DW) factor, which may be probed as a function of angle and therefore probe in-plane and out-of-plane atomic correlations separately.

The measurements show that the DW factor of Ga at the GaSb/AlSb superlattice interface is much higher in the perpendicular direction than in the parallel direction. This anisotropy increases with temperature and decreases with GaSb layer thickness, and for a pure GaSb film the anisotropy is negligible. The experimental results also shown that the DW factors in the parallel direction are similar between GaSb(40 Å)/AlSb(40 Å) and GaSb(20 Å)/AlSb(40 Å), but in the perpendicular direction the DW factor of the GaSb(20 Å)/AlSb(40 Å) is much higher than that of the GaSb(40 Å)/AlSb(40 Å). Although this is not direct evidence, this strongly suggests that the interface initiates the melting process.

X-ray Study of Atomic Correlations in ZnCdSeTe Epitaxial Thin Films	X11A, X23A2
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Q. Lu, B. A. Bunker, H. Luo, A. J. Kropf, K. M. Kemner, J. K. Furdyna

X-ray Absorption Fine-structure Spectroscopy (XAFS) have been performed at approximately 90K to study the local structure of thin films of the II-VI quaternary alloy $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{Se}_{0.5}\text{Te}_{0.5}$. Samples were grown by molecular beam epitaxy (MBE) on (100) GaAs substrates, 4° miscut towards the (111) B direction with a ZnTe buffer layer. The XAFS data indicate that there are more Zn-Se and Cd-Te bonds in the alloy than expected for a random arrangement. The results imply the formation of high-strain local structure and indicate that electronic pairing energies dominate over strain energy. These results are similar to the earlier observation of interlayer switching in ZnTe/CdSe superlattices. Although no long-range ordering is observed in our room-temperature diffraction measurements, the preference of Zn-Se and Cd-Te bonding also implies a tendency to spontaneously form a composition-modulated microstructure.

XANES as a Local Structural Probe *	X11A
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B. Ravel and E.A. Stern (U of Wash.)

We measured the x-ray absorption near-edge structure (XANES) at the titanium K edge on three Ti containing perovskites, EuTiO_3 , PbTiO_3 , and BaTiO_3 . The PbTiO_3 and BaTiO_3 data were collected in fluorescence at room temperature from single domain, single crystal samples. At room temperature PbTiO_3 and BaTiO_3 both possess tetragonal crystal structures. EuTiO_3 is cubic at all temperatures and the data was collected in transmission on a polycrystalline sample. The XANES spectrum is sensitive to the symmetry of surrounding atoms about the transition metal site in transition metal oxides. When the centrosymmetry about the transition metal site is broken, p character from the surrounding oxygen atoms is mixed with the empty d orbitals, allowing a dipole transition with a strength related to the square of the magnitude of the displacement of the Ti atom. In transition metal oxides, this transition appears in the XANES spectrum as a peak in the pre-edge region, shown in Fig. 1 around 4966 eV.

By collecting data on single crystals, we used the polarization of the synchrotron beam to measure the directional dependence of the displacement of the Ti atom in PbTiO_3 and BaTiO_3 . In EuTiO_3 we see no pre-edge peak, consistent with its cubic structure. In PbTiO_3 , we see a strong peak when the electric vector of the x-rays is at a 19° angle to the c -axis ($\text{PbTiO}_3\text{-c}$ in Fig. 1) and a weak peak when entirely perpendicular to the c -axis. The local distortion of the Ti atom in PbTiO_3 is along the long axis of the tetragonal crystal. This is consistent with the measured peaks.

In BaTiO_3 , we see that the pre-edge peak is of similar size when the electric vector forms a 45° angle to the c -axis as when it is perpendicular. Although the crystal is of a tetragonal structure, the local displacement cannot be along the axis of macroscopic polarization. Our results are consistent with chain structure model of Comes et al. [1] In this model, the Ti atom is displaced along one of the $\langle 111 \rangle$, $\langle \bar{1}\bar{1}1 \rangle$, and $\langle 1\bar{1}\bar{1} \rangle$ directions. The vector average of these displacements leads to a tetragonal long range structure. The scalar average is equal in both crystal polarizations, thus the peaks are of similar size.

We have shown that XANES is a direct probe of local distortions in transition metal compounds which yields significant information without the need for extensive analysis. With further analysis, the magnitude of the displacement can be measured and these experiments can be performed as a function of temperature. Thus XANES is a powerful tool for the study of structural phase transitions.

[1] Sol. St. Comm., 6, 715, (1968)

Figure 1. The near-edge peaks of our titanate perovskites.

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R. J. Reeder (SUNY), G. M. Lamble (BNL), J-F. Lee (SRRC), and W. J. Staudt (SUNY)

Analysis of Se-K-edge XAFS spectra of calcite grown from SeO_4^{2-} -bearing aqueous solutions at 25°C reveals the local environment of Se incorporated in calcite. The position of the Se K-edge is consistent with oxidation state 6⁺, and the first shell contains four O atoms at a distance of 1.63 Å, confirming that Se is present as the tetrahedral SeO_4^{2-} complex ion. The second shell is split and is best fitted by approximately 2 Ca atoms at 3.17 Å and approximately 4 Ca atoms at 3.49 Å. The coordination indicated by the split second shell is consistent with substitution of the SeO_4^{2-} ion in the CO_3 site of the calcite, which has six nearest-neighbor Ca atoms. The large size of the SeO_4^{2-} ion and tetrahedral geometry cause significant distortion of the site that is consistent with the observed Se-Ca distances. Two possible models for the local coordination of the SeO_4^{2-} ion are suggested that involve corner sharing of the SeO_4 tetrahedron with neighboring Ca octahedra.

The results suggest that other complex anions - particularly the geochemically important SO_4^{2-} ion, which is also tetrahedral but slightly smaller than SeO_4^{2-} - may also substitute in the CO_3 site of carbonates.

Figure 1. Two possible coordination schemes for SeO_4 substitution in the CO_3 site of calcite. (a) Axial position of the SeO_4 tetrahedron requires a 3+3 split Ca shell and (b) non-axial position requires a 2+4 split Ca shell. We favor the 2+4 split Ca shell of the non-axial position on the basis of its smaller disruption to the anion packing and its more obvious coordination. The analysis also favors (a) but cannot rule out (b).

A. M. Scheidegger, D. L. Sparks (Univ. of Delaware), and G. M. Lamble (NSLS, BNL)

Sorption reactions at the solid-water interface decrease solute mobility and often control the fate, bioavailability and transport of metal ions in soils and groundwaters. A thorough understanding of the structural environment of metals at the solid-water interface is therefore of fundamental importance. In this study, XAFS spectroscopy was used to discern the local atomic structure of Ni(II) sorbed onto pyrophyllite. Pyrophyllite, shows little deviation from the ideal chemical formula $(\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2)$ of 2:1 clays. Its dioctahedral structure consists of essentially neutral tetrahedral-octahedral-tetrahedral layers. Hence, the complexity associated with the permanent charge of planar clay surfaces can be avoided and sorption of ions on pyrophyllite can be ascribed to only edge surface sites. Figure 1 illustrates radial structure functions (RSFs) of Ni treated pyrophyllite samples at pH = 7.5 and at surface sorption densities G, of b.) 3.1, c.) 2.0, d.) 1.0, e.) 0.49, and f.) 0.27 mol m⁻² compared to the spectrum of a crystalline Ni(OH)₂(s) model compound a.). The spectra are uncorrected for phase shift. Note the appearance of a peak at a R of about 2.7 with increasing sorption density. This peak, also present in Ni(OH)₂, represents the second Ni shell and reflects backscattering among multinuclear Ni complexes. Data analysis revealed that the first coordination shell consists of 6 O atoms at 2.02-2.04 Å. For the second shell, XAFS data suggest a single Ni-Al/Si distance (2.96-3.03 Å), indicative of edge sharing of Ni and Al octahedra and possibly the presence of mixed Ni-Al hydroxides. As Ni surface loading on pyrophyllite increased, the number of Ni second-neighbor atoms at a distance of 2.99-3.00 Å increased from N 1 to N 5. The presence of multinuclear surface complexes was depicted at low surface loading and at reaction conditions undersaturated with respect to the formation of Ni(OH)₂(s). This observation suggests that the total coverage of surface sites is not necessary for the formation of multinuclear surface complexes and implies that the pyrophyllite surface promotes hydrolysis and multinuclear complex formation.

1). A.M. Scheidegger, G.M. Lamble, and D.L. Sparks. 1995. Environ. Sci. Technol., in press.

Figure 1. Radial structure functions (RSFs) of Ni treated pyrophyllite samples at various sorption densities compared to the spectrum of a crystalline Ni(OH)₂(s) model compound

Formation of the Ferritin Iron Mineral Occurs in Plastids¹

X11A

G.S.Waldo, E.Wright, Z.H.Whang, J.F.Briat, E.C.Theil, and D.E.Sayers (NCSSU)

Ferritin in plants is a nuclear-encoded, multi-subunit protein found in plastids; an N-terminal transit peptide targets the protein to the plastid, but the site for formation of the ferritin iron mineral is unknown. In biology, ferritin is required to concentrate iron to levels needed by cells ($10^{-7}M$), for above the solubility of the free ion ($10^{-18}M$); the protein directs the reversible phase transition of the hydrated metal ion in solution to hydrated Fe-oxo mineral. Low phosphate characterizes the solid phase iron mineral in the center of ferritin of the cytosolic animal ferritin, but high phosphate in the hallmark of iron mineral in prokaryotic ferritin and plant (pea seed) ferritin. Earlier studies using x-ray absorption spectroscopy (EXAFS) showed that high concentrations of phosphate present during ferritin mineralization in vitro altered the local structure of Fe in the ferritin mineral, mimicking the prokaryotic type, whether the protein was from animals or bacteria. Using EXAFS to analyze the iron environment in pea seed ferritin now shows that the natural ferritin mineral in plants has an Fe-P interaction at 3.26Å similar to bacterial ferritin; phosphate also prevented formation of the longer Fe-Fe interactions at 3.5Å found in animal ferritins or in pea seed ferritin reconstituted without phosphate. Such results indicate that ferritin mineralization occurs in the plastid, where the phosphate content is higher; a corollary is the existence of a plastid iron up take system to allow the concentration of iron in the ferritin mineral.

Large Strain Deformation Study of an Elastomeric Single-Crystal Triblock Copolymer using Synchrotron SAXS

X12B

C. C. Honeker, B. L. Carvalho, E. L. Thomas (MIT) and M. Capel (BNL)

A near single-crystal triblock copolymer with a cylindrical morphology is deformed to large strains with simultaneous measurement of load, sample extension and 2-D small-angle diffraction. The sample is oriented such that the incident beam was directed either parallel or perpendicular to the cylinder axis while stretching in the transverse direction. The p6mm symmetry of the parallel view is immediately reduced to p2mm, which is retained for the remainder of the deformation.

More significantly, the perpendicular view shows that the meridional Bragg scattering changes into a cross as each reflection splits and moves off-axis towards lower q with increasing strain. This latter transformation occurs abruptly at extensions of approximately 110%. Figure 1 shows an X pattern at a deformation of 210%. The local morphology of a deformed sample was examined in direct space using TEM. Figure 2 shows the chevron texture that gives rise to the SAXS pattern of figure 1.

As deformation proceeds the angle between arms of the X pattern increases, reaching an asymptotic value of 145 degrees at the highest deformations (800 percent strain). These SAXS results suggest that upon chevron formation, the cylinders rotate at fixed spacing into an orientation which can best support the applied load.

Present work focuses on synthesizing the SAXS and TEM results in order to construct a 3-D model of the deformed morphology.

Figure 1. SAXS pattern of an oriented triblock copolymer with a cylindrical morphology deformed in a direction transverse to the cylinder axis (vertical). The view direction is perpendicular to the cylinder axis.

Figure 2. Bright field electron micrograph of a sample deformed to 180 percent. The isoprene regions have been preferentially stained dark with osmium tetroxide to provide mass-thickness contrast.

Diffraction Spacing Measurements of Collagen in Turkey Leg Tendon and Rat Tail Tendon *	X12B
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Sidney Lees (Forsyth Dental Center, Boston) and Malcolm Capel (BNL - Biology)

The purpose of this experiment was to determine whether the equatorial diffraction spacing of the collagen in mineralized turkey leg tendon (MTLT) changes when the tissue is immersed in high concentration saline solution (1.5M). Unmineralized turkey leg tendon (UTLT) and rat tail tendon (RTT) were used for comparison. A second comparison was provided by looking at the effect when the tissues were immersed in highly concentrated ethylene glycol solution (3.0M). The objective is to provide further confirmation that there is no mineral between collagen molecules in mineralized tissue, although there are mineral crystallites in the gap regions between linearly joined molecules.

Specimens of the three kinds of tissue were soaked in appropriate solutions while agitated for several weeks at 4C (0.15 M saline, 1.5 M saline and 3.0 M ethylene glycol). The specimen were mounted in sample holders and sealed with 0.005 inch thick Kapton self-adhering film. Equatorial diffraction patterns were digitally recorded using the Brookhaven built crossed wire grid ($\lambda=0.969\text{\AA}$). Corrections for scattering and other effects were made by subtracting the pattern recorded using a blank specimen holder.

No change in spacing was observed for RTT immersed in saline but ethylene glycol induced an increase in the spacing of $1.1\text{\AA}$. However, there was a significant decrease in the spacing for both MTLT and UTLT. Ethylene glycol induced no significant change in the spacing.

UTLT in 0.15M saline: $d = 14.55 \pm 0.11\text{\AA}$;

1.5M saline = $14.03 \pm 0.25\text{\AA}$ Change = 3.6%

MTLT $d = 13.69 \pm 0.12\text{\AA}$;

$13.21 \pm 0.19\text{\AA}$ Change = 3.5%

Since the decrease in spacing is almost the same there can be no mineral between the collagen molecules in MTLT as hypothesized. There is prior evidence that mineral crystallites exist within the gap between colinear collagen molecules.

STRUCTURE OF SEMICRYSTALLINE POLYIMIDES USING REAL-TIME SAXS	X12B
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Sharon X. Lu, Peggy Cebe - Tufts University; Malcolm Capel - BNL Biology

Small-angle X-ray scattering was used to study structure, and the kinetic development of structure in a thermoplastic polyimide, NEW-TPI (Mitsui-Toatsu, Tokyo JAPAN). We performed SAXS measurements of NEW-TPI crystallized either isothermally or non-isothermally from the rubbery amorphous state. The long period, lamellar thickness, and linear crystallinity were obtained from the one dimensional electron density correlation function, which was analyzed according to the method of Strobl and Schneider. SAXS experiments were done at NSLS using a wavelength of 0.154nm , and a sample-to-detector distance of 1.8m calibrated using cholesterol meristate and collagen fiber. The beam profile at the detector is treated according to pinhole geometry. The isotropic SAXS intensity pattern was circularly integrated to increase the signal to noise ratio. Intensity was corrected for changes in the incident beam intensity, sample absorption, background and thermal density fluctuations. The Lorentz corrected intensity was used for data analysis. The one dimensional electron density correlation function was analyzed according to the method of Strobl and Schneider for flat, parallel lamellae. Changes in the long period and lamellar thickness were observed during non-isothermal heating of NEW-TPI from room temperature to the melting point (350 deg. C). Changes were consistent with those seen during high temperature isothermal crystallization. At the beginning of the non-isothermal crystallization process, the crystals are very small and therefore the long period (distance between lamellar stacks) is very large. As temperature increases more and more lamellae are formed, causing a decrease in the average long period. At the same time, already formed crystals are also growing in thickness, and newly formed lamellae are crystallizing at higher temperature. Both effects tend to increase the average lamellar thickness. The lamellar structure formed during non-isothermal crystallization is initially not well organized and can evolve to a more stable structure with either crystallization time, or temperature. In our case, as temperature increases, we observe a slight increase in the long period caused by removal of the thinnest lamellae.

Low-angle x-ray diffraction studies of type II collagen in bovine articular cartilage. *	X12B
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M. Volpi¹, D.W. Chester¹, J.-H. Zhang¹, M.S. Capel², E.P. Katz¹. ¹Univ. Ct. Health Center, Farmington, CT 06030-3705 and ²Brookhaven National Laboratory, Upton, NY 11973

We report the normalized intensities of the first 47 orders (n =order number) of the mostly type II collagen from bovine particular cartilage (BAC) and compare these intensities with those collected from rat tail tendon (RTT) containing mostly type I collagen. 1 mm thick particular cartilage samples, from the femur head, still anchored to the subchondral bone and depleted of proteoglycan were used in all experiments. BAC specimens were totally immersed in buffered saline containing protease inhibitors. In RTT experiments, a small bundle of fibers was kept under slight tension with one end immersed in buffered saline. The first 10-12 orders of fully wet BAC and RTT specimens were collected on beamline X12B. Data from BAC were scaled and integrated with higher order reflections (orders 4- 47) previously collected on beamline X9A. Data from RTT were scaled and integrated with higher order reflections (orders 3-50) collected using an Elliott GX-18 generator with rotating anode and a mirror-monochromator optic. In BAC experiments, a 2D gas and a 2D imaging plate detector were respectively used with specimen to detector (SD) distances of 254.6 cm and 63.3 cm. 2D gas and 2D Siemens detectors were instead respectively used with SD distances of 254.6 cm and 40.0 cm in the RTT experiments. A λ of 1.59 Å was employed in experiments with a SD distance of 254.6 cm and a λ of 1.54 Å was employed in the remaining experiments. Intensities were evaluated by determining the main direction of the meridional axis with an angular integration followed by radial integration of the intensities along this axis. The azimuthal range of integration about the meridional axis was 30 for RTT and 60 for BAC. This difference in integration range was chosen to account for a greater disorder in BAC when compared to RTT. Average disorientation angles of 6 and 16.5 were determined for RTT and BAC respectively using the 5th and 9th order reflections and calculated according to fiber diffraction theory (1). Strip integration, corrected for specimen disorientation and polarization (2), when compared to the previous integration method provided almost identical results. For comparison purposes, an arbitrary value of 1000 was assigned to the first order reflection and all other intensities were subsequently normalized to this value. The intensity functions show many similarities between RTT and BAC. In both systems a very strong first order reflection is followed by strong 3rd, 4th, 5th and 9th reflections. The existence of relatively strong 20th and 21st higher order reflections is also evident. Less striking differences between the two intensity functions seem to occur in a less predictable manner. From these data we have concluded that the $\alpha 2$ chain plays no special role in the molecular packing of type I collagen.

1) Hermans P.H., Contribution to the physics of cellulose fibres. pp. 195-199, Elsevier N.Y. (1946). 2) Wang S.K., Worthington C.R., Biophys. J. 15, 322a (1975).

* Supported by NIH grant AR 37604

Structure of DNA Ligase	X12B
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DNA ligase is the enzyme responsible for ligating Okasaki fragments during the replication of DNA. There are two classes of enzyme, those which use an ATP cofactor and those which utilise NAD⁺. Both classes of enzyme proceed via an adenylated enzyme intermediate. The ATP-dependent enzymes range in molecular weight from over 100kDa for the human type I enzyme, down to 41kDa for the enzyme from bacteriophage T7.

We have cloned, overexpressed and crystallized the T7 ligase. The crystals are of the orthorhombic spacegroup P21212, with one ligase monomer in the asymmetric unit. The crystals diffract to around 2.5Å resolution and data have been collected to 2.7Å on a single frozen crystal on beamline X12B at NSLS. These data have been used for the refinement of the model of the apo-enzyme.

The final structure reveals that the enzyme consists of two domains with a large cleft between them. The active site is in the larger of the two domains. The enzyme appears to operate via a "base-flipping" mechanism which is similar to that proposed for other enzymes, but initially for the HhaI methyltransferase.

Crystallographic Analysis of an Fab Fragment of Anti-Idiotypic Antibody MK2-23 that Mimicks Melanoma Associated Antigen *

X12C

Nenad Ban, John Day, Alexander McPherson (UCR), Xinhui Wang and Soldano Ferrone (NYMC)

Monoclonal antibody MK2-23 bears an internal image of the antigenic determinant defined by anti-high molecular weight-melanoma associated antigen (HMW-MAA) mAb 763-74, and has been shown to induce anti- HMW-MAA immunity in patients with malignant melanoma. It currently sees use as a therapeutic for patients having advanced cases of certain melanoma.

Crystals of the Fab fragment of mAb MK2-23 have been grown from PEG 3350. These crystals belong to the orthorhombic space group $P2_12_12_1$ with unit cell dimensions $a=75.3$, $b=78.2$, $c=83.0$ angstroms. Crystallographic data was collected from one existing crystal at Brookhaven National Laboratory synchrotron. The data to 2.4 angstroms resolution was 5% complete. Crystal structure was determined by molecular replacement using the real space Patterson search method of Huber, as implemented in X-PLOR, with several Fab models as probes. Search results were filtered using Patterson correlation coefficient refinement. The structure of the molecule is currently being refined.

We hope that this study will provide additional insights into the mechanism of molecular mimicry by anti-anti-idiotypic antibodies, and that it will reveal information about the three dimensional structure of the HMW-MAA epitope that is recognized by the idiotype antibody in this cascade.

Report on data collected from TMV protein crystals at NSLS beam-line X12C, April 1-10, 1995.

X12C

Balaji Bhayravhatla and Donald L. D. Caspar (FSU)

Data collection:

Data was collected on crystals of the four layer disk aggregate of tobacco mosaic virus coat protein at pH 8.00. The unit cell parameters of the crystal in space group $P2_12_12_1$ are 220.84 Å in a, 171.70 Å in b and 226.17 Å in c.

Room temperature data was collected using the CCD detector of Walter Phillips (Brandeis University). Low temperature (liquid Nitrogen) data was also collected using the MAR imaging plate available at the beam line. Data was collected in two passes wherever possible. One was a low resolution sweep (1/40 Å to 1/3.5 Å spacing) and the second a high resolution (1/10 Å to 1/2 Å spacing) sweep using both detector systems.

Some long stills and small oscillations were also collected using the MAR imaging plate. The stills were from 300sec to 600sec exposures. The interest is to locate and map any diffuse scattering from the crystals.

Data reduction:

The data collected using the CCD detector has not been processed yet due to some technical difficulties, involving the conversion of the data frames to a DENZO readable format.

The MAR data was collected mostly at LN2 temperatures. Although all the crystals exhibited twinning, we have so far been able to reduce one partial data set. The Rsyms for the data are 5 % to 2.2 Å spacing.

The completeness is only about 20 %. The second partial data set is still being worked on. The twinning of the crystal has prevented us from integrating the data accurately. The Rsyms for the second dataset are around 15 %. Due to this poor statistics we have been unable to merge the two data sets satisfactorily. There are two other partial data sets which will be processed.

A comparison of the 2.2 Å resolution MAR data currently processed to the 2.4 Å resolution cryo data set presently being used to refine the crystal structure gives a scaling of about 11 %. A complete estimate of the quality can be had after we process all the remaining data sets.

One room temperature low resolution data set was collected using the MAR. That data also is from a twinned crystal therefore we are experiencing difficulties in processing. It appears that the two lattices can be separated to obtain two partial data sets. Methods for processing overlapped reflections are being explored.

* This investigation was supported by PHS grants CA37959 and CA5114 awarded by the National Cancer Institute, DHHS and by grants from the NIH (no. GM40706-03), from the NSF and from NASA (NAG-804).

The Structure of Turnip Yellow Mosaic Virus (TYMV)
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X12C

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Turnip yellow mosaic virus (TYMV) is a T=3 icosahedral virus that was discovered in the 1940's. We obtained crystals of TYMV having space group $P6_422$ with unit cell dimensions $a=b=515.5$ Å, $c=309.4$ Å. Native data were collected using a Mar imaging plate at a distance of 615 mm with 0.25 degree oscillations and exposure times ranging from 2 to 6 minutes. In order to increase the resolution of the data collected, the theta arm was set to angles ranging from 5 to 10 degrees, with the maximum resolution being 3.1 Å. The native data were processed and scaled using DENZO and Scalepack, and had an overall completeness of 73% to 3.1 Å with an overall R_{merge} of 10.5%. Heavy atom data were also collected, with diffraction from K_2PtCl_4 derivatized crystals being collected at a wavelength of 1.07 Å to maximize the anomalous signal.

A self rotation function using the native data revealed the orientation of the viral particle in the unit cell. Using Cowpea Chlorotic Mottle Virus (CCMV) as an initial model, molecular averaging was used to improve the phases. An $(F_{PH}-F_P)$ Fourier synthesis using the phases from the averaged map showed that there were icosahedrally related heavy atom sites. The positions of these sites were refined and used to compute native structure factors. After averaging and phase extension, the 3.58 Å map of TYMV showed that the pentameric and hexameric assemblies of the coat protein are prominently protruding from the virion. Work is currently underway to build the amino acid sequence of the coat protein into the electron density.

Figure 1. A 3.58 Å electron density map of the TYMV coat protein at the five fold axis of the virion.

Brief report on data collected from liquid crystalline tobacco mosaic virus specimens at NSLS beamline X12C, June 27-30, 1995.
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X12C

Arunava Chatterjee, Donald L. D. Caspar (FSU), and Dieter Schneider (BNL)

Diffraction data were collected from exceptionally well oriented liquid crystalline specimens of tobacco mosaic virus common and dahlmense strains that had been prepared at Children's Cancer Research Foundation by K. C. Holmes and D. L. D. Caspar in 1959-1960. By tilting the specimens to record high-angle near meridional diffraction, data to 1.25 angstroms resolution was recorded from the best oriented samples. This data is currently being processed to refine atomic models directly against the diffraction data by convoluting model transforms with the experimentally measured specimen orientation distribution and the point-spread function of the recording system.

Using the complete data recorded, including accurate measurement of the low resolution diffraction, difference maps will be calculated between data and refined atomic model to map the partially ordered solvent structure. The data from the dahlmense specimen provides information about the incommensurate periodic perturbation of the helical coat protein structure. It appears from the data recorded from the dahlmense specimens that the perturbation of the protein structure near the outer surface of the virus particle, although regularly periodic, is not very highly ordered.

Development of improved methods of data processing and structure refinement for the TMV fiber diffraction data will provide the most detailed information about structure and solvent interactions of any non-crystalline macromolecular assembly. These methods will be applicable to the analysis of other helical biological assemblies.

The P-state Structure of the Profilin: β -Actin Complex at 2.65 Å Resolution *	X12C
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J.K. Chik (Princeton Univ.), U. Lindberg (Univ. of Stockholm), R.M. Sweet (NSLS), and C.E. Schutt (Princeton Univ.)

While in the crystalline state, β -actin complexed to profilin can undergo structural transitions in response to changes in the crystal bathing solution. The structure of the profilin:actin (P:A) complex in 3.2 M NH_4SO_4 with 10 mM ATP (pH 6.5), the T-state, has been determined [1].

The structure of another crystalline state, the P-state, has now been determined for crystals bathed in 1.8 M KPO_4 with 1mM ATP (pH 7.5). P:A crystals are of $\text{P}2_12_12_1$ symmetry with $a=38.14$ Å, $b=72.45$ Å, and $c=185.7$ Å. Data was 87.3% complete to 2.65 Å with an R_{merge} of 8.2%. The structure was solved by molecular replacement using the T-state model and has been refined to an R-factor of 20.4% with an R_{free} of 33.0%. Compared to the T-state, the P-state actin showed a 9.6 degree opening of the cleft separating the large and small domains and the hydration of previously solvent-excluded ATP phosphates. No divalent cation could be placed with confidence in the P-state structure. Profilin was virtually identical in the two crystal states.

[1] C.E. Schutt, J.C. Myslik, M.D. Rozycki, N.C.W. Goonesekere, and U. Lindberg, Nature 356, 810(1993).

Figure 1. C α trace of P- and T-state β -actin using profilin (not shown) for alignment.

* This work supported by NIH grant GM44038

Crystal and molecular structure of the human adenovirus maturation protease with its 11 amino-acid cofactor	X12C
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J. Ding (SUNY-Stony Brook, Physics), W.J. McGrath, R.M. Sweet, and W.F. Mangel (BNL-Biology)

The three-dimensional structure of the human adenovirus-2 proteinase complexed with its 11 amino-acid cofactor, pVIc, was determined at 2.6 Å resolution by x-ray crystallographic analysis. The fold of this protein has not been seen before. However, it represents an example of either subtly divergent or powerfully convergent evolution, because the active site contains a Cys-His-Glu triplet and oxyanion hole in an arrangement similar to that in papain. Thus, the adenovirus proteinase represents a new, fifth group of enzymes that contain catalytic triads. pVIc, which extends a β -sheet in the main chain, is distant from the active site, yet its binding increases 300-fold the catalytic rate constant for substrate hydrolysis. The structure reveals several potential targets for antiviral therapy.

All diffraction data were measured on the MAR Research 300-mm diameter imaging-plate scanner, mounted on the θ arm of a FAST (Enraf Nonius) diffractometer at Beamline X12C of the NSLS. Native data from one crystal were measured to 2.6 Å resolution with an X-ray wavelength of 1.15 Å; derivative data from three crystals were measured at 1.07 Å (at the peak of the absorption "white line" of heavy atoms in the crystal) to a resolution of 3 Å. The crystals had symmetry $\text{P}6_1$; the unit cell dimensions were $a=b=114.2$, $c=50.1$ Å. The asymmetric unit contained one molecule with a mass of 24,500 Da.

The structure was solved by SIRAS (single-isomorphous replacement with anomalous scattering) from a K_2PtCl_6 derivative. Heavy atoms were located with program HASSP [4]. SIRAS phases were calculated with the PHASES package [2]. Strong phasing power led to a mean figure of merit for 6819 reflections of 0.77. Solvent flattening was performed [5] with PHASES. Amino-acid residues were fitted with program O [3]. The molecular model was refined by conjugate-gradient minimization and simulated annealing with the program X-PLOR [1]. The final residual for 10,500 observations to 2.6 Å resolution was $R_{\text{free}} = 0.23$.

[1] Bruenger, A.T. (1993) X-PLOR, Version 3.1. Yale University. [2] Furey, W. and Swaminathan, S. (1990) Am. Crystallogr. Assoc. Meeting Abstr., PA33, 18, 73. [3] Jones, T.A., Zou, J.Y., Cowan, S.W. and Kjeldgaard, M. (1991) Acta Crystallogr., A47, 110-119. [4] Terwilliger, T.C., Kim, S.-H. & Eisenberg, D. (1987) Acta Crystallogr., A43, 1-5. [5] Wang, B.C. (1985) Methods Enzymol., 115, 90-112.

* This work supported by NIH grant AI26049, the US DOE OHER, and NSF.

Figure 1. Stereo diagram of the folding of the adenovirus protease. The ancillary peptide is shown at the front of the beta sheet.

X-ray crystal structure of the hydroxylase component of methane monooxygenase from <i>Methylosinus trichosporium</i> OB3b.	X12C
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Natesan Elango, R. Radhakrishnan, Wayne A. Froland, Cathleen A. Earhart, John D. Lipscomb and Douglas H. Ohlendorf (University of Minnesota)

Methanotrophic bacteria utilize methane as their sole source of cellular carbon and energy. Methanotrophic oxidation of methane is catalyzed by the enzyme methane monooxygenase [MMO] which is expressed in either a soluble or membrane-bound form. The soluble form of MMO consists of 3 protein components: a hydroxylase [MMOH] (245kDa), a NADH-coupled reductase (38.4kDa), and a regulatory protein called component B (15.8kDa). While all three protein components of MMO are required for efficient oxidation of methane, the MMOH has been shown to contain the active site necessary for activation of molecular oxygen and substrate oxidation[1]. MMOH is a dimeric protein each monomer of which has 3 polypeptide chains ($\alpha\beta\gamma$) of 526, 394 and 168 residues, respectively. Each α subunit contains a μ -hydroxy bridged diiron cluster in its active site. A catalytic mechanism based on reductive activation of dioxygen and homolytic cleavage of the C-H bond of methane (substrate radical intermediate) has been proposed.

MMOH from *Methylosinus trichosporium* OB3b crystallizes in C2221 space group with a monomer ($\alpha\beta\gamma$) per asymmetric unit. The cell dimensions are $a = 264.49\text{\AA}$, $b = 71.16\text{\AA}$ and $c = 139.44\text{\AA}$ [2]. X-ray diffraction data were collected from several single crystals at Brookhaven National Laboratory, beamline X12C at 18°C . The structure was determined by molecular replacement (MR) using a monomer of MMOH from *Methylococcus capsulatus* Bath[3] as the search model. The final R factor of the model for OB3b MMOH is 16.2% for data to $2\text{\AA}$ resolution. The XPLOR program suite was used for both MR and model refinement.

The heart-shaped dimer of MMOH, composed primarily of α helices, sits on a crystallographic 2-fold axis. The diiron cluster is located between 4 long helices of the α chain and is $13\text{\AA}$ under the nearest solvent-exposed surface of the molecule. The irons in each cluster are bridged by 2 hydroxides and both oxygens of a glutamic acid carboxylate. The iron atoms are also coordinated by the N δ of 2 histidines, O ϵ 1 of 3 glutamates, and an exogenous water molecule making both irons hexa coordinate. The geometry of the diiron cluster and the ligand structure are more similar to that seen in flash frozen Bath MMOH [4] than in the search model [3]. This current study has also shown that the published sequence [5] of β chain has 28 consecutive sequence errors near the C terminal region, in addition to another 13 errors randomly distributed over the 3 polypeptide chains. Most notable among these is that Asp209 in the α chain is actually Glu209, a ligand to one of the irons.

[1] Fox, B. G., Froland, W. A., Dege, J. & Lipscomb, J. D. (1989). *J. Biol. Chem.* 264, 10023-10233.

[2] Froland, W. A., Dyer, D. H., Radhakrishnan, R., Earhart, C. A., Lipscomb, J. D. & Ohlendorf, D. H. (1994). *J. Mol. Biol.*, 236, 379-381.

[3] Rosenzweig, A. C., Fredrick, C. A., Lippard, S. J. & Nordlund, P. (1993). *Nature*, 366, 537-543.

[4] Rosenzweig, A. C., Nordlund, P., Takahara, P. M., Fredrick, C. A. & Lippard, S. J. (1995). *Chem. Biol.*, 2, 409-418.

[5] Cardy, D. L. N., Laidler, V., Salmond, G. P. C. & Murrell, J. C. (1991). *Mol. Microbiol.*, 5, 335-342.

High resolution crystal structure of 5' nuclease domain from Taq polymerase	X12C
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Soo Hyun Eom, Jimin Wang, and Thomas A. Steitz (Yale)

After years of prolonged Taq polymerase crystallization incubation, a small crystal form with its largest size of 0.05 mm appeared along with regular intact Taq polymerase crystals. The new crystal form belongs to body-centered tetragonal lattice with its dimensions of $121.6 \times 121.6 \times 75.7\text{\AA}$. An electrophoresis analysis of dissolved crystals indicates that there is a about 33 Kd fragment present in the crystal, a size equivalent to 5' nuclease domain of Taq polymerase. One data set to $2.5\text{\AA}$ resolution was collected on MacScience image system at 1 hour exposure per picture using a home radiation source from a single crystal. Due to low photon counts, an overall merging R-factor for multiple observations was 20.7%. Data were extended to $2.0\text{\AA}$ from the same crystal with the merging R-factor of 6.4% using the NSLS X12C beamline. The exposure per image was 10 minutes, perhaps the longest ever taken at the beamline. The distribution of I/sigma verses resolution suggests that the crystal is likely to diffract to much higher resolution with longer exposures, or stronger beam intensities or larger crystals. We are currently in the process of solving the structure by the molecular replacement method. This structure determination can provide atomic details of the 5' nuclease structure which the intact Taq polymerase only partially provided. In combination with site-directed mutagenesis, we hope to understand the reaction mechanism of 5' nuclease and its functional role in the excision of Okazaki RNA fragments in the lagging-strand DNA replication.

Crystal structure Taq polymerase with a DNA duplex product bound to the polymerase active site.	X12C
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Soo Hyun Eom, Jimin Wang, and Thomas A. Steitz (Yale)

To elucidate the mechanism of DNA polymerase, we have crystallized taq DNA polymerase with a blunt ended DNA duplex at the polymerase active site. The cocrystal is in the same trigonal space group as the apo Taq polymerase. Although they diffracted to 3.5-3.8 Å resolution on a home radiation source, diffraction data have been extended to 3.0 Å at the NSLS X12C beamline.

The complex structure reveals that the DNA duplex binds tangentially to the cleft that is formed by Fingers and Thumb domains, with a 3' terminus to the conserved carboxylates. The first base-pair of the duplex stack against two highly conserved aromatic residues of α helix O with its DNA axis vertical to the α helix. The orientation of the duplex DNA on the polymerase is similar to that observed earlier in an editing complex with Klenow fragment. There are extensive interactions between conserved residues in the polymerase and bound DNA duplex, particularly in the duplex minor groove. These latter interactions may play an important role in promoting the fidelity of this polymerase.

Structure of Allosteric Threonine Deaminase from <i>E. Coli</i> Gilliland, G. & Eisenstein, E. (CARB)	X12C
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The biosynthetic threonine deaminase from *E. coli* is an allosteric tetramer. Each chain comprises 514 residues and one PLP group. Several crystal forms have been analyzed by X-ray diffraction. The unliganded structure is expected to be solved in an orthorhombic crystal form. A synchrotron dataset in a trigonal crystal form was collected from a crystal grown in the presence of excess valine, and is expected to shed light on the allosteric regulation of this enzyme. (Valine is an allosteric ligand.) The crystals of this form grow from 4.4M sodium formate at neutral pH, and belong to space group P3(1)21 with $a=162.5$ and $c=128.7$ and one tetramer in the asymmetric unit. The dataset is 85% complete at 2.9Å resolution with $R_{sym} = 0.11$.

Structure Determination of Transaldolase from E.coli	X12C
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J.Jia, W.Huang, Y.Lindqvist, G.Schneider(Department of Medical Biochemistry and Biophysics, Karolinska Institute, Sweden)

Transaldolase (D-sedoheptulose-7-phosphate:D-glyceraldehyde-3-phosphate dihydroxyacetone- transferase, EC 2.2.1.2) is a ubiquitous enzyme which catalyzes a reversible transfer of a dihydroxyacetone moiety, derived from fructose-6-phosphate to erythrose-4-phosphate yielding sedoheptulose- 7-phosphate and glyceraldehyde-phosphate. The structure was solved with the MIR method using native data and five heavy compound derivative datasets. On beamline X12C using a 30 cm MAR research image plate system, the resolution of the native data set could be increased significantly, from 2.2Å to 1.87 Å. A partial data-set (83% complete from 6.0-1.87Å, R_{sym} 6.2% with no reflections rejected) has been collected. This data merges readily with the native data we collected with a rotating anode as X-ray source(R-merge=8.8%) This merged dataset is 91.3% complete, 82.8% of the total reflections were collected in the highest resolution shell 1.97-1.87Å. This dataset is now used for the final crystallographic refinement of the model solved with the MIR method. The electron density maps calculated with this data-set have improved considerably and consequently, the model of the transaldolase structure is more accurate. The current R-free and conventional R-factor for the protein model are 23.8% and 20.0% respectively.

Structure studies of neurotrophin-3	X12C
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Kelly, J.A. (UCLA), Singer, B. (Amgen), and Yeates, T.O. (UCLA)

Neurotrophin-3 (NT-3) is a member of a family of neurotrophic factors whose function is to promote the survival and maintenance of certain neuronal populations. NT-3 has been crystallized in 2 forms. Orthorhombic crystals, space group P2₁2₁2, diffracted to 2.5Å resolution and have cell dimensions a ≡ 37.97Å b ≡ 51.90Å c ≡ 65.99Å. The second form is space group P4₃2₁2, with cell dimensions a ≡ b ≡ 66.90Å, and c ≡ 108.66Å. The tetragonal crystals diffracted to 2.8Å resolution. Phases for both forms were obtained by molecular replacement using nerve growth factor as the search model.

Crystal structure of *Thermus aquaticus* DNA polymerase

X12C

Youngsoo Kim (Yale, Now in Yeungnam University, Korea), Soo Hyun Eom (Yale), Jimin Wang (Yale), Soo Hyun Eom (Yale), Jimin Wang (Yale), Dae-Sil Lee (Korea Research Institute of Bioscience and Biotechnology), Biotechnology, Biotechnology), Se Won Suh (Seoul National U.) and Thomas A. Steitz (Yale).

The DNA polymerase from *Thermus aquaticus* (Taq polymerase), famous for its use in the polymerase chain reaction, is homologous to *E. coli*. DNA polymerase I (pol I). Like pol I, Taq polymerase has a domain at its amino terminus (residues 1-290) that has 5' nuclease activity and a domain at its carboxy terminus that catalyses the polymerase reaction. Unlike pol I, the intervening domain in Taq polymerase has lost the editing 3'-5' exonuclease activity. Although the structure of the Klenow fragment has been known for ten years, that of the intact pol I has proved more elusive. The crystal structure of Taq polymerase was determined at 2.4 Å resolution using a data set collected on the NSLS X12C beamline; it shows that the structures of the polymerase domains of the thermostable enzyme and of the Klenow fragment are nearly identical, whereas the catalytically critical carboxylate residues that bind two metal ions are missing from the remnants of the 3'-5' exonuclease active site of Taq polymerase. The first view of the 5' nuclease domain, responsible for excising the Okazaki RNA in the lagging-strand DNA replication, shows a cluster of conserved divalent metal-ion-binding carboxylates at the bottom of a cleft. The location of this 5' nuclease active site some 70 Å from the polymerase active site in this crystal form highlights the unanswered question of how this domain works in concert with the polymerase domain to produce a duplex DNA product that contains only a phosphate nick.

Crystal Structure of Fe(III)-Zn(II) Purple Acid Phosphatase with Phosphate Bound to the Active Site

X12C

T. Klabunde, N. Straeter, R. Froehlich, H. Witzel, B. Krebs (Univ. of Muenster)

Purple acid phosphatases containing a dinuclear Fe(III)-Me(II) center (where Me can be Fe or Zn) in their active site catalyse the hydrolysis of activated phosphoric acid esters and anhydrides like ATP, at a pH range from 4 to 7. The characteristic purple color of this subclass of acid phosphatases results from a tyrosine to Fe(III) charge transfer transition at approximately 560 nm. Interactions with phosphate, which is a competitive inhibitor of the phosphatase activity, have been investigated in several spectroscopic studies in order to understand the detailed mechanism of ester hydrolysis. The X-ray structure of the dimeric 111 kDa Fe(III)-Zn(II) kidney bean purple acid phosphatase (kbPAP) with phosphate bound to the active site has been determined at a resolution of 2.7 Å using the structure of the native enzyme as a starting model [Straeter, N., Klabunde, T., Tucker, P., Witzel, H., and Krebs, B. (1995) *Science*, 1489-1492]. Furthermore the data for the native structure could be improved to 2.65 Å. In native kbPAP the iron ion is coordinated by Tyr-167, His-325, and Asp-135 and the zinc ion by His-286, His-323, and Asn-201. The two metals are bridged monodentately by Asp-164. In the inhibitor complex the oxyanion binds in a bidentate bridging mode to the two metal ions, replacing two of the presumed solvent ligands present in the native enzyme form. As also proposed for the native structure a bridging hydroxide ion completes the coordination spheres of both metal ions to octahedral arrangements. In the phosphate-enzyme complex the third and the fourth oxygen atom of the phosphate group interact with the imidazolium cations of His-202 and His-296. Both structures are consistent with a mechanism of phosphate ester hydrolysis involving a nucleophilic attack on the phosphorus by an Fe(III)-coordinated hydroxide ion. The negative charge evolving at the phosphorus in the assumed penta-coordinated intermediate might be withdrawn by the two metal ions and by His-202 and His-296.

Figure 1. Active site region of kbPAP displaying the metal coordinating ligands

Crystal Structure Determination of L-aspartate- β -semialdehyde dehydrogenase (ASADH, E.C. 1.2.1.11)	X12C
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Kryger, G., Petsko, G.A. and Ringe D. (Brandeis University)

The enzyme L-aspartate- β -semialdehyde dehydrogenase (ASADH, E.C. 1.2.1.11) is an NADP-linked dehydrogenase that is encoded by the *asd* gene in *Escherichia coli*. The reaction catalyzed by this enzyme, which reversibly converts L-aspartate- β -semialdehyde to L- β -aspartyl-phosphate, is located at a key branch point in the metabolic pathway of aspartate to other amino acids.

To understand the mechanism and specificity of ASADH better, its three dimensional crystal structure determination was carried out by single isomorphous replacement and multiple wavelength anomalous diffraction methods. ASADH crystals are extremely sensitive to radiation damage caused by the x-rays, they diffract poorly in a home-lab x-ray source, and only one heavy-atom derivative was found after extensive searches (the Hg atom in PCMB). These crystal characteristics made it imperative that the data will be collected at a wavelength-tunable, very intense, x-ray source. This was achieved at the Brookhaven National Laboratories NSLS X12-C, run by Dr. R. Sweet. The structure was solved using three datasets collected at this beam line, one native at a resolution of up to 2.6Å, and two datasets at different wavelength from a single Hg derivatized crystal at 3.0Å. Data were collected from the two crystals at cryogenic temperature. The structure determination is at the initial model fitting stage at the time this abstract is written.

Crystal Structure of the A Domain from the a subunit of Integrin CR3 (CD11b/CD18)	X12C
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Jie-Oh Lee, Robert Liddington (DFCI, HMS)

Integrins are plasma membrane proteins that mediate adhesion to other cells and to components of the extracellular matrix. The interactions of several integrins with their extracellular ligands are mediated by an A-type domain (generally called the I-domain in integrins). We have determined the high resolution crystal structure of the I-domain from the a chain of integrin CR3. The domain adopts a classic a/b "Rossmann" fold and contains an unusual Mg²⁺ coordination site at its surface. One of the coordinating ligands is the glutamate side chain from another I-domain molecule. We suggest that this site represents a general metal ion-dependent adhesion site (MIDAS) for binding protein ligands. We further propose that the b subunits of integrins contain a MIDAS motif within a modified I-domain. Our crystal structure will allow reliable models to be built for other members of the I-domain superfamily and should facilitate development of novel adhesion modulatory drugs.

METHODS: The structure was solved using multiwavelength dispersion (MAD) technique with a selenomethionine derivative. All the MAD data and high resolution native data were collected on beam line X12C. Data were processed to an R_{sym} 3-4% and completeness is 99%. MAD phase were determined to 2.0Å resolution using program MLPHARE (overall figure of merit=0.65). The structure was refined to an R factor of 21% at 1.7Å resolution with good geometry. The final model contains all non-hydrogen atoms of residues D132 to K315 and 150 water molecules.

Two conformations of the integrin A-domain (I-domain): a pathway for activation?	X12C
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Jie-Oh Lee, Robert Liddington (DFCI, Harvard Medical School)

Integrins are a family of cell adhesion molecules expressed on cell surface. Most integrins are rapidly and reversibly activated in response to agonists, leading to highly regulated cell adhesion. This activation is associated with conformational changes in their extracellular portions. The interactions of several integrins with their ligands are mediated by a type A-domain (generally called the I-domain in integrins). We have described previously the structure of a 'liganded' I-domain grown in the presence of Mg²⁺, and now report the structure of an 'unliganded' form grown in the presence of Mn²⁺. Comparison of the two crystal form reveals a change in metal coordination which is linked to a large (10Å) shift of the C-terminal helix and burial of two phenylalanine residues within the hydrophobic core of the Mn²⁺ form. Our observations provide the first atomic resolution view of conformational changes in an integrin domain, and suggest a link between these structural changes and a change in adhesiveness.

METHODS: Data were collected to 2.0Å resolution on beam line X12C using a MarResearch imaging plate, with wavelength of 0.98Å. Data are 99% complete and R_{sym} is 6% (27% in outer shell). The structure was solved by molecular replacement using the Mg²⁺/I-domain structure as the search model. The structure was refined using XPLOR and manual model building to a final R factor of 21%. The final model comprises all non-hydrogen atoms of residues D132 to A318 and 100 water molecules.

Crystal structure of a Lyme-disease antigen in complex with an antibody.	X12C
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Hong Li and Catherine L. Lawson Biology Department, Brookhaven National Laboratory

Borrelia burgdorferi is the organism responsible for Lyme disease on Long Island. OspA is an abundant surface protein of the *Borrelia* spirochete that has been found to trigger immunopathological processes. To aid in vaccine development for Lyme disease, the crystal structure of OspA and its complex with the Fab fragment of a monoclonal antibody (Fab184.1) is being determined.

Recent efforts have focused on collecting higher resolution native data and heavy atom derivatives (Pt and I). A mutant form of recombinant OspA (Ser69 → Cys69) has allowed the growth of larger crystals (0.14mm x 0.1 mm x 0.6 mm). In addition, suitable conditions were found to freeze the crystals in a nitrogen gas stream. A native data set to 2.3 Å was collected at the X12C beamline of the NSLS, and a Cys69 data set to 1.9 Å was collected at the X25 beamline.

A partially refined OspA-Fab184.1 model was obtained by tracing an electron density map calculated with a combination of multiple isomorphous replacement and molecular replacement phases. The protein backbone trace for OspA was confirmed by difference Fourier between two Ser → Cys single mutants and the wild type OspA data sets, and by a platinum site near the sole methionine residue of OspA.

The current protein model consists of residues 7-257 of OspA (28 kD) and all residues of Fab184.1 (50 kD) with an overall isotropic temperature factor. The crystallographic residual factor R is 29% and free R is 37%. Further refinement of the model is currently underway.

The secondary structure of OspA is in qualitative agreement with results obtained by circular dichroism studies [1] at beamline U9. OspA consists mostly of β-sheet with one α-helix (the last 9 residues). OspA is composed of two domains, an N-terminal β-sheet domain (residues 1-116) and a partially closed C-terminal β-barrel domain (residues 117- 257).

[1] France, L. L.; Kieleczawa, J.; Dunn, J. J.; Hind, G. and Southerland, J. C. (1992). *Biochim. et Biophys. Acta* 1120:59-68.

Figure 1. Partially refined structural model of OspA-Fab184.1. OspA is represented by ribbon model.

Structural studies of Stearoyl-acyl Carrier Protein Desaturase from Castor Seed	X12C
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Stearoyl-acyl Carrier Protein Desaturase(EC 1.14.99.6) catalyzes the first desaturation step of stearyl-ACP resulting in oleoyl-ACP. The dimeric delta-9 desaturase consists of 363 amino residues per subunit and contains a diiron center. The structure of the enzyme was solved using a single derivative in combination with 6-fold averaging to 3.2Å resolution. On beamline X12C, the resolution could be extended to 2.4Å and the obtained dataset is 87% complete, Rmerge 0.075. The refinement of the model against this data-set is currently underway. The significant increase in resolution has been critical in obtaining a reliable protein model and would not have been possible using conventional X-ray sources.

Viral Protein VP16	X12C
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Y.Liu, C. Huang, W. Herr, and X. Cheng (Cold Spring Harbor Laboratory, Cold Spring Harbor, New York 11724)

The herpes simplex virus (HSV) encoded protein VP16 is not only an essential structural component of the HSV virion, but also the activator of HSV immediate-early (IE) gene expression. VP16 is one of the most potent transcriptional activators identified in eukaryotes. It forms a multiprotein complex with cellular proteins Oct-1 and HCF to activate viral IE gene transcription by binding to TAATGARAT elements in the IE promoters. This binding enables the activation domain of VP16 to interact with the basal transcriptional machinery and activate transcription of the viral IE genes. Therefore, structural studies of VP16 will lead to an understanding of multiprotein-DNA interactions involved in transcriptional regulation. Since transcription regulation is intimately related to cell growth, cell cycle control, and oncogenesis, VP16 has been a subject of intensive studies. A three-dimensional crystal structure of VP16 will not only shed light on the mechanism of VP16 function, but also facilitate further biochemical characterization of the protein.

A construct encoding a GST-fusion with the central region (amino acids 48-412) of VP16 that is sufficient for VP16 induced complex formation but lacks the activation domain has been made. The fusion protein was purified on a glutathione-agarose column, and VP16 was released from the fusion by thrombin digestion at the junction between the GST and VP16 sequences. Thrombin and VP16 were then separated by Q-sepharose column chromatography. Purified VP16 was crystallized by the hanging-drop method into rod-like crystals with an average dimension of 0.2 x 0.2 x 1.0 mm³ at 16°C. Preliminary results indicate that the VP16 protein crystallizes into an orthorhombic space group with unit cell dimensions of a=60 Å, b=77 Å, c=83 Å. The crystals diffract X-ray beyond 3 Å and the structural determination is underway.

M. O'Gara (Cold Spring Harbor Lab.), R.J. Roberts (NEB), X. Cheng (Cold Spring Harbor Lab.)

In 1993, we solved and published the structure of the M.HhaI-AdoMet complex (Cheng et al., 1993). From this binary structure determined at 2.5 Å resolution, we learned that the M.HhaI folds into two broad domains: a catalytic domain that contains catalytic and cofactor-binding regions, and a DNA-recognition domain. Later, we solved and published the ternary structure for a chemically-trapped covalent reaction intermediate between the M.HhaI, a duplex 13-mer DNA oligonucleotide containing methylated 5-fluorocytosine at its target and reaction product AdoHcy (Klimasauskas et al., 1994). This structure determined at 2.8 Å resolution reveals the three-dimensional basis for the functions of amino acids implicated in DNA-sequence specificity, catalysis and cofactor binding. The DNA is bound in a cleft between the two domains. The structure is the first to demonstrate "an amazing distortion in DNA induced by a methyltransferase", i.e., the substrate nucleotide is completely flipped out of the helix during the modification reaction. The structure also provides a clear example of induced-fit for both protein and the DNA in the sequence-specific substrate binding by M.HhaI.

The above ternary structure represents one step of the reaction pathway. During the past year, we crystallized, collected, and solved structures of M.HhaI with cognate DNA and methylated DNA, in the presence of S-adenosyl-L-homocysteine. The structures of these two complexes have been refined to crystallographic R-factors of 0.189 and 0.178, respectively, at 2.7 Å resolution. The two structures reveal that (1) both unmethylated 2'-deoxycytidine and 5-methyl-2'-deoxycytidine completely flip out of the DNA helix and fit into the active site of the enzyme, (2) the C5 methyl group of the flipped 5-methyl-2'-deoxycytidine lies in between the C5 and the sulfur of S-adenosyl-L-homocysteine, (3) two water molecules, held near the hydrophobic edge of the flipped cytosine (C5 and C6) by two conserved amino acids (Gln-82 and Asn-304) and the phosphoryl oxygen of the phosphate group 3' to the flipped nucleotide, may serve as the base for the elimination of the proton from C5, and (4) the protonation of ring N3 of the cytosine during the methylation reaction may occur through a water-mediated interaction between the terminal carboxyl group of Glu-119 and the amino group of the methionine moiety of S-adenosyl-L-methionine.

Cheng, X., Kumar, S., Posfai, J., Pflugrath, J.W., Roberts, R.J. (1993) *Cell* 74, 299-307. Cheng, X., Kumar, S., Klimasauskas, S., Roberts, R.J. (1993) *Cold Spring Harbor*

Symp. Quant. Biol. 58, 331-338. S. Klimasauskas, S. Kumar, R.J. Roberts, and X. Cheng. (1994) *Cell* 76, 357-369.

S. Kumar, X. Cheng, S. Klimasauskas, S. Mi, J. Posfai, R.J. Roberts, and G.G. Wilson. (1994) *Nucleic Acids Res.* 22, 1-10. X. Cheng (1995) *Curr. Opin. Struc. Biol.* 5, 4-10. X. Cheng (1995) *Annu. Rev. Biophys. Biomol. Struct.* 24, 293-318. M. O'Gara, K. McCloy, T. Malone, and X. Cheng (1995) *Gene* 157, 135-138. G. Schluckebier, M. O'Gara, W. Saenger, and X. Cheng (1995) *J. Mol. Biol.* 247, 16-20. Malone, T., Blumenthal, R.M., Cheng, X. (1995) *J. Mol. Biol.* 253, 618-632.

M. O'Gara, S. Klimasauskas, R.J. Roberts, and X. Cheng. submitted

G. Privé (University of Toronto/OCI) and D. Eisenberg (UCLA)

α_1 is a peptide designed to form an α -helix and self-assemble into a four-helix bundle. The 2.7 Å resolution structure of the peptide at pH 3.4 has been reported (Hill et al., *Science* 249, 543-546 (1990)) in which the peptides form α -helices as predicted, but these associate into a complicated network of dimers, trimers and hexamers in the crystal lattice. A second crystal form has been obtained at neutral pH. These crystals adopt space group P1 and have unit cell dimensions of $a=20.8\text{Å}$ $b=20.9\text{Å}$ $c=27.1\text{Å}$ $\alpha=102.4^\circ$, $\beta=95.3^\circ$, $\gamma=119.6^\circ$, containing four crystallographically unique peptides. Since the triclinic crystals diffract to better than 1.5Å resolution on a conventional rotating anode x-ray source, attempts were made to collect an ultra-high resolution data set on beamline X12C for *ab initio* phasing via the Shake-and-Bake method. This method can solve structures with several hundred atoms if atomic resolution data are available.

A single crystal was frozen at 100 Kelvin and used for all data collection. Monochromatic radiation at $\lambda=0.92\text{Å}$ was used throughout, and the 150 mm radius Mar Research imaging plate detector was positioned at a crystal to detector distance of 130 mm and $2\theta=12^\circ$ in order to collect the highest resolution data possible. Two different crystal orientations were required to completely cover the hemisphere of unique data, and both short and long exposures were needed to measure the full dynamic range of the data. In total, 77,116 observations were reduced to 23,681 unique reflections using Denzo/Scalepack, with an R_{merge} of 0.076 (100.00% complete ∞ -1.40Å ; 83.4% complete 1.40-0.92Å). Shake-and-Bake was able to solve 10% of random-atom trial starting structures. The final structure consists of 450 non-hydrogen atoms (408 peptide atoms), and has been refined with SHELXL-93 to an R value of 0.12 for all data to 0.92Å and an R_{free} of 0.14. The four unique peptides form antiparallel arrays of α -helices, thus fulfilling one of the main design goals. Unexpected interhelical associations also occur, generating head-to-tail stacks of helices throughout the lattice, with alternating layers of hydrophobic and ionic zones.

Figure 1. 2Fo-Fc electron density map

Figure 2. View down helix axis

Crystallographic Studies of Adenylosuccinate Lyase from <i>B. subtilis</i>	X12C
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Matthew Redinbo, Todd O. Yeates; University of California, Los Angeles

Adenylosuccinate lyase (ASL) from *Bacillus subtilis* is a 200 kDa homotetramer that catalyzes two steps of de novo purine biosynthesis leading to the formation of AMP and IMP, both steps involving the beta-elimination of fumarate. A single point mutation in the human ASL gene has been linked to mental retardation with autistic features, and ASL also plays an important role in the bioprocessing of anti-HIV therapeutics. Recombinant *B. subtilis* ASL, which shares 70% sequence identity with human ASL, has been crystallized. Diffraction on an in-house Rigaku generator with an R-Axis IIc imaging plate yielded data to 3.8 Å resolution for crystals frozen to 100 K. Data collection at beamline X12C at the NSLS at Brookhaven National Laboratory extended the resolution to 3.3 Å, also using crystals frozen to 100 K (Rmerge=6.1%, 93% complete, $\langle I \rangle / \langle \sigma \rangle = 5.4$ for data between 3.4 and 3.3 Å resolution). *B. subtilis* crystals are of space group P6122 or P6522 and have a relatively long c-axis of approximately 280 Å. The MAR detector at beamline X12C mimics three circle geometry and allowed the orientation of the c*-axis approximately along the phi (rotation) axis which facilitated the collection of a complete, higher resolution data set. Structure determination by multiple isomorphous replacement is in progress, and we consider the higher resolution data collected at X12C to be a crucial step in the progress of the structure determination of *B. subtilis* ASL.

High-Resolution X-Ray Diffraction Data of Gene V Protein of bacteriophage f1.	X12C
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Gene V protein (GVP) of bacteriophage f1 is involved in DNA replication. It binds to single-stranded nucleic acids with high affinity but little sequence specificity. GVP coats single-stranded DNA during bacteriophage f1 replication, forming an ordered superhelical protein-DNA complex. This protein-DNA complex facilitates packaging of the ssDNA into new phage particles. The GVP is a member of the OB-fold superfamily of proteins.

The X-ray Crystallographic structure of GVP has been determined by our laboratory at 1.8 Å. GVP is a dimer with identical subunits. The monomer of GVP forms a distorted five stranded anti-parallel beta barrel. The protein portion of GVP has been used to model the single-stranded DNA into a left-handed superhelical complex. In addition, the structure of GVP is being used to study protein stability by determining crystal structures of site-directed mutants in the core of the protein.

We recently extended the high-resolution X-ray diffraction data of GVP to 1.4 Å at beamline X12C (Fig 1.). The data are of excellent quality with a Rsym on I of 5.3%. Data is complete to 96% and protein atomic refinement is under investigation.

Gene V protein X12C data collection 25 Aug 1995

Figure 1. A portion of the film plate showing X-ray Diffraction to 1.4 Å.

Structure of the Actin:Profilin:Rhodamine-phalloidin Complex *	X12C
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N. Vogelaar (Princeton Univ.), U. Lindberg (Stockholm Univ.), R.M. Sweet (NSLS), and C.E. Schutt (Princeton Univ.)

One of the main goals of our laboratory is to understand the nature and structure of actin—its conformational flexibility, how it binds to other proteins, and the manner in which it self-associates to form microfilaments. Toward these ends, our lab has determined the structure of the “T-state” actin:profilin complex [1]. In that structure, we observed extensive actin-actin interactions and speculated that they may be related to contacts in the actin filament. The current work supports this hypothesis in that we have demonstrated using confocal fluorescence microscopy that rhodamine-phalloidin binds to actin:profilin crystals. Phalloidin is known to bind and stabilize actin filaments but does not interact significantly with actin monomers. Data from a single, frozen, rhodamine-phalloidin-soaked actin:profilin crystal was collected and was 94% complete to a resolution of 2.3 Å. The R_{sym} was 8.1%. The space group is $P2_12_12_1$, with cell constants of $a=37.69$ Å, $b=71.77$ Å, and $c=187.33$ Å. Molecular replacement was done using the “P-state” actin:profilin structure [2] using 8-4 Å data. The crystallographic residual using the resulting model was 35%. Preliminary results indicate that the actin cleft is more open than the “T-state” structure, but more closed than the “P-state” structure. Although the rhodamine-phalloidin site has not yet been determined, both the ATP and the calcium ion have been tentatively placed. Refinement is continuing.

[1] C.E. Schutt, J.C. Myslik, M.D. Rozycki, N.C.W. Goonesekere, and U. Lindberg, *Nature* 356, 810(1993).

Crystal structure of the DNA polymerase from phage RB69, an α family and replication polymerase.	X12C
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Jimin Wang (Yale), A. K. M. Sattar (Yale), Jim Karam (Tulane), W. H. Konigsberg (Yale) and Thomas A. Steitz (Yale)

T4 DNA replication is one of the best studied systems. All of ten T4 encoded components at the replication fork have been cloned and overexpressed and subject to extensive biochemical and biophysical studies. The center component of the replicase, the gene 43 product (gp43) or T4 DNA polymerase, is the enzyme responsible for DNA synthesis. T4 DNA polymerase is a pol α family polymerase, to which eukaryotic polymerases belong. T4 DNA polymerase possesses two enzymic activities, 5'-3' polymerase and 3'-5' exonuclease, in addition to its ability to bind its own mRNA as autogenous translation regulation.

Bacteriophage RB69 is a distant relative of T4 phage family. Many of RB69 encoded proteins show high similarity with T4 proteins. Their gp43 or DNA polymerases share 62% identity and 75% similarity.

The crystal structure of RB69 DNA polymerase has been solved at 3.8 Å resolution in an orthorhombic space group ($P2_12_12_1$) using two mercurial derivatives, and at 5.0 Å in a monoclinic space group ($P2_1$) using one mercurial derivative using a home x-ray radiation source. The diffraction data have been extended to 2.8-3.1 Å for the orthorhombic space group using 10 crystals and to 3.2-3.5 Å for the monoclinic from 6 crystals using the intense x-ray radiation source at the NSLS X12C beamline. The structure has then been extended to the resolution limits using non-crystallographic averaging procedures among one copy of molecule in $P2_12_12_1$ and two copies in $P2_1$.

The crystal structure of RB69 DNA polymerase reveals that the polymerase consists of five domains called amino terminal (N), 3'-5' exonuclease (Exo), Fingers, Palm and Thumb. Domains N and Exo are located at the amino terminus and possesses 3'-5' exonuclease activity, respectively. Both domains are within the first 388 amino acids, whose structure was previously solved as a fragment of the T4 DNA polymerase. The remaining carboxy terminal polymerase domains form a cleft that contains three catalytically important carboxylate residues located at the bottom of this cleft. The Palm domain containing these carboxylates has an identical topology as Palm domains of the HIV reverse transcriptase and the Klenow fragment of pol I. The fingers and thumb domains, however, have structures that are unique to the corresponding parts of the other DNA polymerases of known structures. Four of five domains (N, Exo, Palm and Thumb) are arranged within a plane, and the fifth domain (Fingers) with 50 Å long helices protruding at the back. In comparison to the relative positioning of the 3'-5' exonuclease to the polymerase in the Klenow fragment, the exonuclease domain in RB69 DNA polymerase has been translocated from the template strand side to the primer strand side of the presumed bound DNA duplex product.

* Supported by NIH grants GM44038 and AI30743

Casein kinase I

X12C

R. Xu, G. Carmel, J. Kuret, and X. Cheng (Cold Spring Harbor Laboratory, Cold Spring Harbor, New York 11724)

Casein Kinase I (CKI) is a serine/threonine specific protein kinase that is ubiquitous in eukaryotic organisms. Last year we solved the structure of the catalytic domain of CKI from *Schizosaccharomyces pombe* in complex with MgATP at 2.0 Å resolution (Xu et al., 1995). The crystals were formed in a trigonal space group (P3221). This year, we solved the crystal structure of CKI complexed with an inhibitor CKI7, refined to a crystallographic R-factor of 17.8 at 2.5 Å resolution.

A large family of isoquinoline sulfonamide compounds inhibits protein kinases by competing with ATP, yet interferes little with the activity of other ATP-using enzymes such as ATPases and adenylate cyclases. One such compound, N-(2-aminoethyl)-5-chloroisoquinoline-8-sulfonamide (CKI7), is selective for CKI isolated from a variety of sources. The CKI-CKI7 structure provides new insights into the mechanism of the ATP-competing inhibition and the origin of their selectivity toward different protein kinases. Selectivity for kinases versus other enzymes is achieved by hydrophobic contacts and the hydrogen bond with isoquinoline ring. We propose that the hydrogen bond involving the ring nitrogen-2 atom of the isoquinoline must be preserved, but that the ring can flip depending on the chemical substituents at ring positions 5 and 8. Selectivity for individual members of the kinase family is achieved primarily by interactions with these substituents.

References:

- G. Carmel, B. Leichus, X. Cheng, S.D. Patterson, U. Mirza, B.T. Chait, and J. Kuret. 1994. *J. Biol. Chem.* 269, 7304-7309.
 R. Xu, G. Carmel, R.M. Sweet, J. Kuret, and X. Cheng (1995) *EMBO J.* 14, 1015-1023.
 R. Xu, G. Carmel, J. Kuret, X. Cheng. submitted

Report on data collected from insulin and osteogenic protein (OP-1) crystals at NSLS beamline X12C, April 1-10 and June 27-30, 1995.

X12C

Bin Yu and Donald L. D. Caspar (FSU)

Anomalous difference low resolution data were collected from cubic insulin crystals soaked in 1M tungstate buffer to map the distribution of ions in the solvent space in April. Measurable anomalous differences were observed out to 9 Å spacing. The result was presented in ACA 95 meeting (Abstract M001). The datasets are being used in conjunction with other contrast variation experiments to map the solute accessible space in cubic the insulin solvent which occupies 67 % of the crystal volume.

Complete data (1/80 Å to 1/2.4 Å spacing) from native OP-1 protein with intact disordered N-termini were collected in June. In collaboration with Dr. D. Griffith, the project is to map the disordered N-terminal segment (about 40 residues) by including low resolution data. Analysis is in progress.

MAD data at 3 wavelengths from 2-Zn crystal soaked in 0.1M Tl+ were collected at LN temperature to 1.25 Å spacing in June. Binding of Tl+ near B13 was noted by Blundell and Johnson in their textbook. However there was no evidence of such binding under the conditions of this experiment. The quality of the data is exceptional and comparison with published structure (refined to 1.5 Å) is in progress.

X-ray Diffraction Study of Tilted Phases of Langmuir Monolayers * X14A

M.K. Durbin, A. Malik, A.G. Richter, R. Ghaskadvi, and P. Dutta (Northwestern University), and Thomas Gög (Oak Ridge National Lab)

We used grazing incidence diffraction to study tilted phases of Langmuir monolayers, and discovered a new phase in which the molecules tilt in a non-symmetry direction. We were also able to observe the transition from a tilted phase with ordered backbone planes to one with disordered backbone planes. We studied arachidic (C_{20}) acid and nonadecanoic (C_{19}) acid along a 0°C isotherm, and along a 15dynes/cm isobar. The isotherm passes through four different phases. Each phase has a different tilt symmetry. Figure 1 shows the tilt magnitude and orientation (azimuth) as a function of pressure. The highest pressure phase is untilted (U). As the pressure is lowered, the molecules begin to tilt towards a next-nearest neighbor (NNN tilt, $\phi = 30^\circ$). The third phase has intermediate tilt (I tilt, $30^\circ > \phi > 0^\circ$), and the lowest pressure phase has nearest neighbor tilt (NN tilt, $\phi = 0^\circ$).

The isobar remained entirely within the NN phase, but it has been suggested that the NN phase be subdivided into two phases. At low temperatures, the molecules are expected to have a herringbone packing, whereas at high temperatures they should have no orientational order. The orientational order and the tilt both contribute to a distortion of the hexagonal lattice. The distortion can be measured, and the effect due to tilt subtracted out. The distortion due entirely to orientational ordering of the molecules is plotted in Figure 1. There is a clear transition near 30°C from non-zero distortion to no distortion.

Figure 1. Tilt behavior of C_{20} acid along a 0°C isotherm.

Figure 2. Distortion due to molecule backbone ordering along a 15dyn/cm isobar.

* This work was supported by the U.S. Dept. of Energy grant no. DE-FG02-84ER45125.

Atomic Resolution Imaging with Multi-Energy X-ray Holography (MEXH) X14A

T. Gog (ORNL), P.M. Len, C.S. Fadley (UC Davis), D. Bahr, C. Sanchez-Hanke, G. Materlik (HASYLAB)

Multi-energy x-ray holography (MEXH) is introduced as a new technique for directly imaging atomic structures in the bulk or at surfaces of solids. It utilizes monochromatic synchrotron radiation incident on the sample to generate an internal scattering field and monitors fluorescence from specific atoms to determine the electric field strength at the center of these atoms. Scanning an extended volume of reciprocal space and converting the resultant intensity distribution by Fourier transform, a real space image of the immediate atomic environment around an emitter is obtained.

MEXH can be regarded as the x-ray equivalent to multi-energy electron emission holography and as an inversion of the more conventional idea of x-ray fluorescence holography (XFH). In contrast to XFH, however, image aberrations known to drastically distort single energy holograms are effectively suppressed by this multi-energy approach.

MEXH was applied to a natural slab of single-crystal Hematite (Fe_2O_3), which consists of alternating layers of iron and oxygen and can be conveniently described as a hexagonal lattice. The figure below shows a real-space reconstruction of an iron (0,0,1) layer in Hematite. Clearly to be seen are iron atoms on the six nearest sites neighboring a central emitter as well as atoms on corner sites of the underlying hexagonal grid, up to distances of about 8Å

Figure 1. Holographic reconstruction of an iron (0,0,1) layer in Hematite (Fe_2O_3)

X-ray Fluorescence Holography: Imaging the Atomic Environment in Hematite (Fe_2O_3)	X14A
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T. Gog (ORNL, HASYLAB), P.M. Len, C.S. Fadley (UC Davis), D. Bahr, C. Sanchez-Hanke, G. Materlik (HASYLAB)

To study the feasibility of x-ray fluorescence holography (XFH) as a tool for directly imaging atomic environments in solids, an attempt was made to resolve the structure in the immediate vicinity of Fe atoms in a natural Hematite (Fe_2O_3) crystal. Choosing four different energies above the K-absorption edge of Fe and varying the direction of the incident beam on the sample following a $5^\circ \times 5^\circ$ grid in polar and azimuthal angles, Fe $K\alpha$ fluorescence was collected at more than 1400 points in $\vec{k}$ -space. After a careful background subtraction procedure, specific crystal planes in $\vec{r}$ -space were reconstructed by Fourier transformation of the $\vec{k}$ -space data.

Multi-Energy X-ray Holography: Images of Ge(100)	X14A
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T. Gog (ORNL), R.H. Menk, F. Arfelli (BNL), P.M. Len, C.S. Fadley (UC Davis)

While initial efforts to record multi-energy x-ray holograms (MEXH) from Hematite were very encouraging, several experimental issues need to be addressed to fully realize the potential of this new method. One special concern are excessive data acquisition times, which were of the order of 150 hours in the case of Hematite.

In the current study it was attempted to image the structure of an ideal Ge(100) crystal. A major improvement in counting capability came through the use of a fast proportional counter with associated fast preamplifier, discriminator, pulse converter and scaler. Energy dispersion was accomplished with a curved graphite analyzer. Maximum count rates in this single channel set-up were in excess of 300000 s^{-1} , at a total detector dead time of approximately 200 ns, as determined within the frame of non-extended dead time theory. With these characteristics, sufficient holographic data could be recorded at four different energies above the Ge $K\alpha$ absorption edge in a substantially reduced time of about 48 hours.

The figure below is a rendering of a preliminary holographic reconstruction of the Ge(100) plane. Four corner atoms around the central emitter mark the cubic unit cell of the diamond structure. With measured distances of approximately 5.5 Å between pairs of corner atoms, these atomic positions are in reasonably good agreement with the published lattice constant of 5.66 Å.

Figure 1. Holographic reconstruction of the Ge(100) plane

Study of Surface Active Poly(pyrroles) using Synchrotron X-ray Diffraction *	X14A
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T. Herod, G. Weekaseekra, T. Servay, and R.S. Duran (University of Florida), M. Durbin, A. Malik, and P. Dutta (Northwestern University)

Previous investigations which reported the successful imaging of polypyrroles using Scanning Tunneling Microscopy (STM) triggered our interest in further elucidating the structural organization of these polymers in monomolecular layers. One way of improving the informational content of an STM image would be to disrupt the periodicity along the polymer chain. To accomplish this we prepared copolymers of 3-hexadecyl pyrrole (3HDP) and N-octadecyl pyrrole (NOP). The different substitution would allow for the resolution of the monomer units and to locate the polymer backbone. As an aid in this investigation, the structure of the polymer, copolymer, and corresponding monomers, were investigated at the air-water interface using synchrotron x-ray diffraction. X-ray measurements were performed at the Oak Ridge National Laboratory on beamline X14 of the National Synchrotron Light Source. The experimental setup has been described in previous publications.

Langmuir films of the pure 3HDP and a mixture of 50:50 (m) 3HDP and NOP were prepared at a temperature of 25°C and a surface pressure of 5 mN m⁻¹. Diffraction data was acquired for each of these systems. Interpretation of these results are still being formulated. One off-plane diffraction peak ($K_z = 0.10-0.50 \text{ \AA}^{-1}$) was seen at $K_{xy} = 1.46 \text{ \AA}^{-1}$ for the pure 3HDP and two off-plane peaks, 1.47 and 1.44 $\text{\AA}^{-1}$ were seen for the mixed monomer system. Interpretation of these results are still pending. Polymerization of the pure monomer, and mixtures, were accomplished via chemical oxidation with 0.03 M ammonium persulfate on the water surface for 70 minutes, with a constant surface pressure of 5 mN m⁻¹. The surface pressure was then increased to 20 mN m⁻¹ and x-ray data acquired. Single (triply-degenerate) in-plane diffraction peaks were seen for the homopolymer and the copolymer at 1.47 $\text{\AA}^{-1}$. This data supports the model of a 2-dimensional hexagonal lattice with lattice constant of 4.9 $\text{\AA}$ with the alkyl chains standing normal to the water surface.

Figure 1. Diffraction of poly(3-Hexadecylpyrrole) at the air-water interface.

* Supported in part by ONR, and Micron Semiconductor, Inc.

Inelastic X-Ray Measurements of the Local-Field Factor for a Simple Metal	X14A
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B. C. Larson (ORNL)

Recent first principles calculations by Fleszar et al.⁵ have shown that band structure effects are responsible for the double peak in the dynamic structure factor $S(q,w)$ for aluminum. Their results suggested that detailed measurements of $S(q,w)$ as a function of energy loss w and wave vector q near twice the Fermi wave vector, 2 kF, could now be used to get information on the physics of short-range electron correlations in simple metals. The X-14 beam line at the National Synchrotron Light Source has been used to measure $S(q,w)$ near 2kF for aluminum as shown in Fig. 1. The measurements are compared to ab initio calculations of $S(q,w)$ in order to obtain experimental insight into the details of the (static) Hubbard-like many-body local field factor, $G(q)$. In the figure, the curves labeled So refer to non-interacting electron-hole pairs propagating in the band structure of aluminum. The RPA, TDLDA, and TDHF curves refer to calculations for three different forms of $G(q)$: RPA corresponds to mean-field calculations where $G(q) = 0$; the TDLDA curves refer to a time-dependent extension of the local density approximation in which $G(q) \propto q^2$; and the TDHF curves refer to a $G(q)$ (derived from time-dependent Hartree-Fock calculations⁶) that is strongly peaked at $q \approx 2$ near 2 kF. There is remarkable agreement between the TDHF calculations and the measurements up to 2 kF, indicating that $G(q)$ for aluminum reaches a value 2. A value this large rules out most existing models for $G(q)$, and the departure from TDHF above 2 kF requires additional work. Direct fitting of $G(q,w)$ as a dynamic local field factor is in progress.

Figure 1. X-ray measurements and theoretical calculations of the dynamical structure factor for aluminum along the 013 direction. The open circles denote the measurements and the lines represent calculations as defined in the legend.

X-Ray Measurement of the Local-Field Factor for Aluminum

X14A

B. C. Larson (ORNL), J. Z. Tischler (ORNL), E. D. Isaacs (AT&T Bell Labs), P. Zschack (ORNL), A. Fleszar (University of Würzburg), and A. G. Eguluz (University of Tennessee and ORNL)

Recent first principles calculations [1] have suggested that band structure effects are responsible for the double peak in the dynamic structure factor $S(\vec{q}, \omega)$ for aluminum. The calculations suggested further that detailed measurements of $S(\vec{q}, \omega)$ as a function of energy loss ω and wave vector q near twice the Fermi wave vector, $2k_F$, could now be used to get information on the physics of short-range electron correlations in simple metals. The X-14 beam line has been used to measure $S(\vec{q}, \omega)$ near $2k_F$ for aluminum as shown in Fig. 1. The measurements are compared to ab initio calculations of $S(\vec{q}, \omega)$ in order to obtain experimental insight into the details of the (static) Hubbard-like many-body local field factor, $G(q)$. In the figure, the curves labeled S_0 refer to non-interacting electron-hole pairs propagating in the band structure of aluminum. The RPA, TDLDA, and TDHF curves refer to calculations for three different forms of $G(q)$: RPA corresponds to mean-field calculations where $G(q) = 0$; the TDLDA curves refer to a time-dependent extension of the local density approximation in which $G(q) \sim q^2$; and the TDHF curves refer to a $G(q)$ (time-dependent Hartree-Fock calculations [2]) that is strongly peaked with magnitude ~ 2 near $2k_F$. There is remarkable agreement between the TDHF calculations and the measurements up to $2k_F$, indicating that $G(\vec{q}, \omega)$ for aluminum reaches a value ~ 2 . A value this large rules out most existing models for $G(q)$, and the departure from TDHF above $2k_F$ calls for additional work. Direct fitting of $G(\vec{q}, \omega)$ as a dynamic local field factor is in progress.

- [1] A. Fleszar, A. A. Quong, and A. G. Eguluz, Phys. Rev. Lett. 74, 590 (1995).
- [2] F. Brosens and J. T. Devreese, Phys. Stat. Sol. (b) 147, 173 (1988).

Figure 1. X-ray measurements and theoretical calculations of the dynamical structure factor for Al along the [013] direction.

Control of the colony microstructure of high T_c superconductors

X14A

E.D. Specht, A. Goyal, D.M. Kroeger (ORNL), J.A. DeLuca, J.E. Tkaczyk, and J.A. Sutliff (GE)

$Tl_1Ca_2Sr_2Cu_3O_{10}$ (Tl-1223) high- T_c superconductors grown on polycrystalline substrates have been shown to have high critical current densities (J_c) even at high temperatures and in high magnetic fields. Because polycrystalline substrates are used, these results make Tl-1223 a promising material for high-current applications requiring long lengths of wire, such as power transmission, magnets, generators, and motors.

The high J_c has been shown to result from local crystallographic alignment in the films[1]. While the films have no global in-plane alignment, "colonies" of aligned grains can be as large as a mm, containing thousands of grains. While high J_c has been reported within a single highly-aligned colony, optimum J_c over long lengths requires an in-plane, intracolony mosaic of ~ 20 deg. FWHM.

Tl-1223 films are grown by exposing a precursor material to Tl_2O vapor[2]. Microdiffraction[3] was used to analyze the average colony size and mosaic as a function of the exposure time (Fig. 1) and the Tl_2O flow rate (Fig. 2). An optimum colony size was produced by using a low flow rate and long exposure time, which leads to a complete reaction at a slow rate.

- [1] E.D. Specht et al., Physica C 242, 164 (1995).
- [2] J.A. DeLuca et al., Physica C 205, 21 (1993).
- [3] E.D. Specht et al., Physica C 226, 76 (1994).

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Figure 1. Dependence of colony mosaic on time exposed to Tl_2O

Figure 2. Dependence of colony mosaic on Tl_2O flow rate

X-ray diffraction of human brain neuromelanin and synthetic neuromelanin. *

X14A

Q.J. Wang, M. Eisner, P.R. Crippa, S.C. Moss (Physics Dept., University of Houston) P. Zschack, T. Gogg (ORSL/NSLS Beamline X14) L. Zecca (I.T.B.A.-CNR, Milan, Italy)

Four samples were studied in both transmission and reflection (high- q). The first sample is natural human neuromelanin consisting of a pressed powder disk of 3mm in diameter and 0.15mm in thickness. The second sample is enzymatic neuromelanin synthesized at Houston. The third sample is auto-oxidized dopamine melanin with Fe^{3+} ions, while a fourth sample is auto-oxidized neuromelanin with Fe^{3+} ions. The three synthetic samples are disks of 10mm in diameter and about 1mm in thickness. The X-ray photon energy at X14 was chosen at 16KeV. The proposed molecular formula of these samples is essentially $\text{C}_{73}\text{H}_{102}\text{N}_8\text{O}_{32}\text{S}_3\text{Fe}$. We may note that the first sharp peaks of all three synthetic neuromelanins are between $q=1.6\text{\AA}^{-1}$ and $q=1.7\text{\AA}^{-1}$ while the first sharp peak of the human brain neuromelanin is at $q=1.32\text{\AA}^{-1}$. These peaks have in the past [1] been associated with interplanar order. In addition the synthetic samples have more detailed structure compared with the natural sample at higher q . Nonetheless the higher- q data seems similar in all which indicates that they have similar planar structures.

These raw data sets are being processed to remove the measured Compton scattering (through the use of X14 analyzer/PSD detector) and are being reduced to provide $S(q)$ for further analysis.

1. J. Cheng, S.C. Moss, M. Eisner and P. Zschack, Pigment Cell Res. 7 255 (1994), 7,263 (1994)

Figure 1.

* Research at Houston was supported by the U.S. DOE/BES on contract DE-FG05-87ER 45325.

X-ray Standing Wave Measurements of a Metal/Polymer Interface * X15A

M.J. Bedzyk (ANL and Northwestern U.), B. DeKoven (Dow Chemical), P.F. Lyman (Northwestern U.), and M. Radler (Dow Chemical)

There are a growing number of technological interests in the optical, electronic, magnetic, and catalytic properties of structures derived from thin metallic films evaporated on polymeric films. We are developing the use of x-ray standing waves (XSW) as an in-situ, chemically sensitive structural probe for profiling these structures. As a trial, the morphology and possible thermal diffusion of a thin Cu layer deposited on a siloxane-based polymer film that coated a Au mirror was studied with XSW. The results suggest that the thin Cu film forms 'islands' when deposited and that the projected width of the Cu distribution changes after annealing. The diffusion of Cu into the polymer film is less than 5 Å before and after annealing.

The long-period XSW was generated above the Au mirror surface by total external reflection (TER). The XSW period ($D = \lambda/2\sin\theta$) is infinite when the beam is parallel to the plane of the mirror, and shortens at finite angles. At the critical angle (θ_c) the period is $D_c = 80$ Å for Au. Figure 1 depicts the data and fit for a sample with a thin Cu layer (~ 2 Å) deposited on a ~ 500 Å film at room temperature. The oscillations in the reflectivity (Kissig fringes) reveal the thickness of the film (530 Å) and roughness of the two interfaces (4 Å). The striking oscillations in the Cu K fluorescence occur when the extrema of the XSW move past the Cu layer. Assuming a Gaussian profile, the model curve indicates the Cu film is $\langle z \rangle = 531$ Å above the Au surface with a projected width of 23 Å. If the Cu layer were uniformly 2 Å thick and perfectly parallel to the Au surface, the Cu modulations would not be noticeably attenuated at higher angles within the TER region (since 2 Å is small compared to the XSW period). The observed damping is most likely due to Cu islanding. After vacuum annealing to 300°C for 1 hour (with no Cu loss), there is no significant change in the modulation period indicating that the Cu distribution has the same average height $\langle z \rangle$ above the Au mirror (Fig. 2). However, the Cu modulations are now stronger at higher angles, indicating that the thickness of the Cu layer as projected along the surface normal has decreased to 14 Å.

* Sponsored in part by the US DOE (BES-DMS), under contract W-31-109-ENG-38, and by the NSF under contract to the MRC at Northwestern U.

The Use of X-ray Standing Waves and Evanescent-Wave Emission to Study Buried Strained-Layer Heterostructures *

X15A

T.-L. Lee (Northwestern U.), Y. Qian (Northwestern U. and ANL), P.F. Lyman (Northwestern U.), J.C. Woicik, J.G. Pellegrino (NIST) and M.J. Bedzyk (Northwestern U. and ANL)

A heteroepitaxial structure consisting of 1 ML InAs grown on GaAs(001) and subsequently capped with 25 Å GaAs was examined by the x-ray standing wave (XSW) method. By monitoring the In L fluorescence while scanning through the GaAs(004) Bragg reflection, the indium position is measured to be 0.22 Å above the nearest GaAs(004) diffraction plane (Fig. 1). This corresponds to a perpendicular strain of 7.7% within the InAs layer, which is in good agreement with macroscopic elasticity theory (7.3%). We also demonstrate that, by limiting the emission takeoff angle α_u of the observed As L α fluorescence, the evanescent-wave-emission effect can be used in conjunction with the XSW method to determine the strain-induced displacement of the cap layer in the growth direction (Fig. 2). This displacement (0.47 Å) is measured to be twice the displacement of the indium layer.

Figure 1.

Figure 2.

* This work was sponsored by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract W-31-109-ENG-38, and by the NSF under contract to the MRC at Northwestern University.

Surface Structure of Submonolayer Phases of Sn/Si(001) *

X15A

Paul F. Lyman (Northwestern U.) and Michael J. Bedzyk (Northwestern U. and ANL)

Adsorption of $\sim$ monolayer quantities of Sn on the Si(001) surface results in a rich surface phase diagram of LEED superstructures [1]. A striking STM investigation strongly suggests that these phases are constructed from various arrangements of a few basic structural building blocks; specifically, highly buckled dimers are prevalent on the surface [2]. To understand the chemical composition and local geometrical structure of these surface phases, we undertook an x ray standing wave (XSW) investigation of the known phases of Sn/Si(001). Our results appear to bear out the STM hypothesis that the local structure of the various phases is similar.

For coverages below 0.75 ML, our results are most consistent with the presence of Sn-Sn dimers, buckled by about 13°. For this buckling angle, the two Sn atoms of the dimer are nearly out of phase from one another with respect to the (004) reflection XSW. This manifests itself as a low value of the (004) Sn coherent fraction, but a reasonably high (022) Sn coherent fraction (see Fig. 1). Above 0.75 ML, the (004) coherent fraction increases abruptly, which is due to a sharp change in the buckling angle (to $< \sim 10^\circ$) and/or to occupancy of the second Sn layer. These second layer sites are certain to be populated upon exceeding a monolayer.

[1] K. Ueda, K. Kinoshita, and M. Mannami, Surf. Sci. 145, 261 (1984). [2] A.A. Baski, C.F. Quate, and J. Nogami, Phys. Rev. B 44, 11167 (1991).

Figure 1. Sn coherent fractions and coherent positions from (004) and (022) XSW scans as a function of Sn coverage for Sn/Si(001)

* This work was sponsored by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract W-31-109-ENG-38, and by the NSF under contract to the MRC at Northwestern University.

Paul F. Lyman (Northwestern U.) and Michael J. Bedzyk (Northwestern U. and ANL)

Adsorption and growth of Sn on Ge surfaces represents a highly mismatched ($\sim 15\%$) case of IV-IV epitaxy. Stemming from the fact that the diamond-structure allotrope of Sn (gray, or α -Sn) is a zero-gap semiconductor, alloys of Sn and Ge are predicted to have useful and interesting electronic properties, such as a direct band gap and high carrier mobilities. However, the equilibrium solid solubility of Sn in Ge is quite low, and metastable alloys are difficult to construct even by MBE methods due to rapid segregation of Sn to the growth front. We have begun to explore the possibility of employing a surfactant species (i.e., one having a low surface energy) to kinetically suppress the ability of the Sn to segregate during Ge overgrowth and to thus construct metastable SnGe multilayers or alloys.

We undertook an x-ray standing wave (XSW), low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES) investigation to study the feasibility of surfactant-mediated epitaxy. By using Bi as a surfactant species, we suppressed the segregation mobility of the Sn heterolayer during subsequent Ge overgrowth (measured by AES). Fig. 1 depicts the XSW fluorescence modulation from the Bi overlayer after various SnGe growths. This renders a direct measure of the Bi adsorption height relative to the bulk lattice planes (c.f. table of coherent positions in Fig. 1); owing to the larger lattice spacing of Sn, the adsorption height is increased upon Sn growth, but remains unchanged (up to a modulus of the lattice d-spacing) upon Ge overgrowth. These facts firmly establish that the Bi surfactant does indeed segregate to the surface. Furthermore, our XSW measurements reveal a well-ordered ($>70\%$) Sn heterolayer after ~ 20 ML Ge overgrowth in the presence of a surfactant.

Figure 1.

* This work was sponsored by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract W-31-109-ENG-38, and by the NSF under contract to the MRC at Northwestern University.

Yonglin Qian and Michael J. Bedzyk (ANL and Northwestern U.)

In an earlier study of the structure of the Ga/Si(001) surface, we had found that Ga adsorbs at room temperature as a dimer, residing above unbroken Si dimers, and oriented parallel to those dimers [1]. In the present work, we have employed fundamental (004) and higher-order harmonic (008) x-ray standing wave (XSW) measurements (Figs. 1a and 1b) to directly measure the lattice positions and thermal vibrational amplitudes of Ga ad-atoms on a 0.3 ML Ga/Si(001) surface. The Ga adatom vibration amplitude along the surface normal direction was thereby determined to be 0.135 ± 0.01 Å. Furthermore, by reducing the uncertainty of the vibrational amplitude, this result allows us to determine the Ga ad-dimer bond length (measured previously using an (022) reflection) with much higher accuracy (2.58 ± 0.04 Å) than in our previous studies.

[1] Y. Qian, M.J. Bedzyk, S. Tang, A.J. Freeman, and G.E. Franklin, Phys. Rev. Lett. 73, 1521 (1994).

Figure 1. Experimental data and best fit for the fluorescence yield and reflectivity versus θ for: (a) the (004) reflection and (b) the (008) reflection.

* This work was sponsored by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract W-31-109-ENG-38, and by the MRC at Northwestern U., under contract to the NSF.

An X-ray Standing Wave Study of Surface Kinetics: Bismuth Adsorption on Si(001) *

X15A

Y. Qian (ANL and Northwestern U.), P.F. Lyman, T.-L. Lee (Northwestern U.) and M.J. Bedzyk (ANL and Northwestern U.)

It has been theoretically predicted that the stable phase for Bi adsorption on the Si(001) surface is coverage-dependent, with a (1x2) phase stable at coverages $\theta > 0.5$ ML, and a (2x2) phase stable for coverages $\theta < 0.5$ ML [1]. To test these predictions, we used the x-ray standing wave (XSW) technique to experimentally investigate the temperature- and coverage-dependent surface structure and reaction kinetics of Bi adsorption on the Si(001) surface.

We deposited 0.2 ML of Bi on the Si(001)-(2x1) at room temperature. Subsequently, we acquired a series of (004) XSW measurements after annealing to various temperatures (Fig. 1). The (1x2) and (2x2) phases possess markedly different adsorption heights [1], and so fractional surface phase compositions of the (1x2), (2x2) and a disordered phase could be determined from these high resolution measurements (Fig. 2). The (2x2) Bi phase that is predicted to be the low coverage structure was found to be a metastable phase. It undergoes an irreversible phase transition to the stable (1x2) phase upon annealing. The thermal activation energy of 0.4 ± 0.2 eV and exponential prefactor of 10^{-1} Hz for the (2x2)-to-(1x2) transition were determined from the conversion rate at different temperatures. This experiment demonstrates a new approach for investigating the kinetics of surface transitions.

[1] S. Tang and A. J. Freeman, Phys. Rev. B 50, 1701 (1994).

Figure 1. A series of (004) XSW measurements after isochronal anneals.

* This work was sponsored in part by the US DOE, BES-DMS, under contract W-31-109-ENG-38 and by the MRC at Northwestern U under contract to the NSF.

Figure 2. Derived fractional phase compositions of Bi vs. annealing temperature.

Surfactant-assisted growth of Ge on Si(111)

X15A

J.C. Woicik (NIST), P.F. Lyman (Northwestern), and M.J. Bedzyk (Northwestern and ANL)

The x-ray standing wave technique, Auger-electron spectroscopy, and low-energy electron diffraction have been applied to the study of Bi surfactant-assisted growth of Ge on Si(111). The original Bi-terminated Si(111) surface is found to exhibit a $\sqrt{3} \times \sqrt{3}$ R30 LEED pattern, and the Bi position, 0.97 d Si(111), corresponds to the sum of the Bi and Si covalent radii for Bi atoms directly atop the Si atoms of the first Si layer. Upon submonolayer deposition of Ge, the Bi adatoms are displaced up to the surface, and Ge grows on the Si surface as a coherent, strained double layer. The Bi segregation is evidenced by an increase in the Bi adsorption height, as measured by XSW, and the fact that there is no reduction in Bi Auger intensity or change in the LEED pattern. Evidence for the Ge double layer are the measured Ge coherent fraction ($F = 0.64$) and position ($P = 1.08$). In contrast, the expected parameters for an unstrained perfect crystalline Ge double layer having the Ge lattice parameter would be $F = 0.71$ and $P = 1.04$, respectively.

Quantifying Zn Doping in InGaAsP/InP Laser Structures	X15B
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L. Niu, R. F. Karlicek, and P. H. Citrin (AT&T Bell Laboratories)

Precise control of dopant concentrations, which is generally important in fabricating semiconductor devices, is particularly critical for Zn-doped InGaAsP/InP laser structures operating in the 1.3 - 1.5 μm range. Too much Zn (typically $\geq 2 \times 10^{18}$ atoms/cc) leads to excessive diffusion into the active layer, increasing lasing thresholds and reducing efficiency, while too little Zn causes carrier leakage around that layer, degrading its high temperature performance. Such low doping levels and tight tolerances require highly sensitive and precise diagnostics, characteristics well matched to the conventionally used technique of SIMS. Using improved fluorescence detection capabilities, we have applied NEXAFS to a variety of Zn-doped InP structures and shown that this approach provides substantially higher precision than SIMS and has the additional benefit of being non-destructive. We have also established that there is a well-defined concentration regime in which substitutional occupation of Zn is linearly proportional to Zn exposure. Apart from determining more reliable growth parameters in the fabrication of these high performance diode lasers, our findings demonstrate the general utility of x-ray absorption spectroscopy for non-destructive quantification of dilute dopants in semiconductors.

X-ray Absorption from Pb-modified Fluoride Glasses	X15B
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L. Niu, A. R. Kortan, and P. H. Citrin (AT&T Bell Laboratories)

ZBLAN fluoride glasses (Zr/Ba/La/Al/Na), with theoretical ultra-low optical losses at near-infrared wavelengths, suggest potential applications in optical fibers and in hosts for optical lasers and amplifiers. After two decades of study, however, there is very limited structural understanding of these materials. Useful applications demand an adjustable range of refractive indices, which are obtained by partial substitution of some of the elements of ZBLAN. Lead is the most popular substituent for Ba, but above critical Pb concentrations the stability of the glass significantly decreases. To understand this phenomenon, ZBLAN glasses have been studied using NEXAFS and EXAFS. It was found that only at Ba sites and only under unstable glass conditions (i.e., high Pb concentrations) are structural and electronic changes observed. These changes indicate that the glass stability is almost exclusively related to the local structure of the Ba atoms, which are believed to modify the glass by randomly occupying the interstitial sites of the ZrF_6 -polyhedra network, thereby increasing the corner sharing with respect to edge sharing.

Structural Characterization of Cr^{4+} -YAG Crystals Lasing at 1.5 μm	X15B
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L. Niu, L. F. Schneemeyer, T. D. Harris, and P. H. Citrin (AT&T Bell Laboratories)

A new laser material, Cr^{4+} - $\text{Y}_3\text{Al}_5\text{O}_{12}$, has been studied as a potential source for optical communications at 1.5 μm . Solid-state lasers typically offer advantages of reliability, noise, and cost. The novelty and challenge of this material lies in overcoming the natural tendency of dopant Cr^{3+} ions to substitute both tetrahedral and octahedral Al^{3+} sites and favor instead, using co-dopants such as Ca^{2+} for charge compensation, substituting optically active Cr^{4+} ions on only Al^{3+} tetrahedral sites. Optimization of crystal growth parameters for achieving this is made difficult by the lack of suitable structural characterization methods. Chromium and calcium K -edge EXAFS experiments have been used to identify the concentration of Cr^{4+} , Cr^{3+} , and Ca^{2+} in different environments as a function of various growth parameters. Preliminary results have already ruled out the role of several parameters that had been believed to be significant.

Size and Composition of Luminescent Oxidized Si Nanocrystals	X15B
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S. Schuppler, L. E. Brus, and P. H. Citrin (AT&T Bell Laboratories)

The study of nanosized systems is of growing interest, particularly in materials involving Si because of their potential applications to optoelectronic technology. As part of a broad program to identify and characterize the visibly luminescent species in anodically grown (H-passivated) porous Si, we have investigated size-selected fractions of luminescent Si nanocrystals prepared from pyrolysis of disilane with subsequent oxidation in O_2 . The optical and structural properties of these nanocrystals, ox-Si $_n$, made them ideal model systems for studying luminescence activity because of their chemical inertness (due to the outer oxide shell) and their simple spherical shape (determined from TEM imaging). However, since particles luminescing in the visible region with outer diameters ≤ 30 Å are beyond imaging or diffraction capabilities for determining internal structure and composition, x-ray absorption measurements were required. We obtained Si K -edge NEXAFS data from four size-selected groups of ox-Si $_n$ particles with mean outer diameters of 96, 45, 33, and 26 Å. In each group a small but discernible feature was observed approximately midway between the well-separated (~ 7 eV) absorption edges of the Si $_n$ and SiO $_2$ components, corresponding to incompletely oxidized Si at the Si $_n$ -SiO $_2$ interface. From the relative edge jumps and densities of the three components and from the outer diameters of the spherical particles, the mean inner diameters of the Si $_n$ cores and thicknesses of the interfacial SiO $_x$ and outer SiO $_2$ layers were determined. The outer diameters varied a factor of 4 and the corresponding core diameters of 78, 31, 17, and 11 Å varied a factor of 7, but the SiO $_2$ - and SiO $_x$ -layer thicknesses of 6.5 and 1.5 Å remained remarkably constant. These findings, coupled with the varying luminescent energies of the different sized particles, convincingly ruled out earlier suggestions that either SiO $_2$ or SiO $_x$ is the optically active species. Instead, our results showed that it is the inner Si $_n$ cores which are responsible for the optical activity. The dimensions of these cores and the strong similarity of their luminescent behavior to that observed in a series of porous Si samples proved essential in characterizing these latter heterogeneous and more chemically reactive materials.

Cation Charge State and Local Structure in the Rare-earth Fulleride $\text{Yb}_{2.75}\text{C}_{60}$	X15B
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S. Schuppler (AT&T Bell Labs), E. Ozdas (Hacettepe U.), K. B. Lyons, A. R. Kortan, and P. H. Citrin (AT&T Bell Labs)

Recently discovered electron-donor intercalated C_{60} fulleride compounds have received much attention because of their extraordinary physical properties. Most notably, record high superconducting temperatures for organic systems have been observed in alkali-metal fullerenes, prompting exploration for other elements as donors. Superconductivity has so far been demonstrated in monovalent alkali-metal donor compounds $(\text{K}, \text{Rb}, \text{Cs})_3\text{C}_{60}$ and divalent alkaline-earth donor compounds Ca_5C_{60} and $(\text{Sr}, \text{Ba})_6\text{C}_{60}$. Expanding the search to the predominantly trivalent rare-earth (RE) metals has resulted in only one reported case of successful donor intercalation, $\text{Yb}_{2.75}\text{C}_{60}$, which becomes superconducting below 6 K.

We have obtained NEXAFS measurements from the single-phase form of this rare-earth fulleride which indicate that the cation is exclusively divalent. EXAFS data have also been obtained which show that there exists strong local ordering of the surrounding C_{60} molecules. Two well-defined average Yb-C nearest-neighbor distances separated by $0.18 \pm 0.03 \text{ \AA}$ were observed, corresponding to the Yb(II) cations occupying off-centered octahedral and tetrahedral interstices of the f.c.c. C_{60} sublattice. Heating $\text{Yb}_{2.75}\text{C}_{60}$ above 670°C was shown to produce an amorphous carbide phase containing Yb(III). Our results, combined with thermodynamic arguments and analogues in organometallic compounds, have been used to explain the observed single-crystal structure of $\text{Yb}_{2.75}\text{C}_{60}$ and to infer expectations for forming fullerenes with other RE metals.

Identifying Point Defects in Si-doped GaAs using NEXAFS and EXAFS	X15B
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S. Schuppler, L. N. Pfeiffer, K. W. West, and P. H. Citrin (AT&T Bell Laboratories)

The problem of electrical deactivation, i.e., the decrease (trapping) of active carriers due to defects with increasing donor concentration, is encountered in all semiconductors, but it is particularly severe in GaAs highly doped with Si, its most common *n*-type dopant. Amphoteric Si can occupy both *n*-type Ga sites (Si_{Ga}) and *p*-type As sites (Si_{As}), so the electrical deactivation has generally been attributed to acceptor-Si atoms trapping free-electron carriers. Using NEXAFS data to measure directly the upper limit concentration of Si atoms occupying such *p*-type As sites, we showed last year that only about half of the observed electrical inactivity was due to this autocompensation mechanism. Identification of the dominant defects responsible for the additionally missing carriers was made this year using EXAFS. Analysis of data obtained from $\text{Si}_x\text{Ge}_{1-x}$ model systems ($x = 0.03, 0.20, \text{ and } 0.50$) and comparison with data from highly Si-doped GaAs revealed a comparatively large number of both neutral $\text{Si}_{\text{Ga}}\text{-Si}_{\text{As}}$ dimers and small Si_n clusters. The relative concentrations of these two point defects, along with the two monomer defects Si_{Ga} and Si_{As} , were found to depend on the total Si doping level and the orientation of the GaAs surface during growth.

Diffraction study of an etched InP grating

X16A

K. Evans-Lutterodt (AT&T) and P. Imperatori (ICMAT-CNR)

Many interesting structures are manufactured with features on the mesoscopic length scale, and cannot be characterized by standard, non-destructive optical techniques, due to wavelength limitations of the optical probes. Diffraction techniques may be useful, if the structure is periodic, and if the coherence length of the diffractometer exceeds the period sufficiently. Diffraction techniques measure statistical properties of the sample, which may some times be the parameters of interest.

We have studied a lithographically etched array of lines on the (100) surface of an InP crystal. Shown are scans near the (4,-4,2) Bragg peak. Scans a, b and c are at $L=2.00$, 1.99 and 1.98 respectively.

Two features are apparent. The period of the grating corresponds to the oscillations visible at $L=1.99$ and 1.98. However it is clear, particularly at $L=1.98$, that there are two broad additional side lobes. By monitoring these side lobes as a function of L , we have identified these as due to (111) facets. Our interpretation is that the sidewall of the grating is not perpendicular to the interface as it would be in a square wave, but the sidewalls are (111) facets corresponding to a truncated sawtooth shape for the grating.

Figure 1. Diffracted intensity as function of H , for constant L .

Structural study of the ZnSe/GaAs interface

X16A

P. Imperatori (ICMAT-CNR, Italy), K. Evans-Lutterodt (AT&T Bell Labs.) and R. Felici (ISM-CNR, Italy)

Heterovalent semiconductor heterojunctions such as ZnSe/GaAs present a remarkable correlation between the interface composition in the early growth stage and the final value of the valence band offset. In order to better understand this correlation, an x-ray diffraction study of the ZnSe/GaAs interface was performed. We investigated a set of samples grown by molecular beam epitaxy, with a different Zn/Se beam pressure ratio (0.1, 1 and 10 respectively) and having the same thickness (50 Å). For each sample we measured the crystal truncation rod scattering at different photon energies, just above and below the k-edges of Zn, Ga, As and Se, in order to change the atomic scattering factors and better separate the contribution of each element to the atomic structure of the interface. Figure 1 shows one of the measured rod at two different energies. We also looked for reconstruction peaks at the interface, due to the presence of possible (Ga,Se) interfacial compounds, but no evidence of such peaks was found. Data analysis to determine the atomic arrangement at the interface is currently underway.

Figure 1. Intensities of the (00L) rod for incident photon energies below (solid line) and above (dashed line) the Zn k-edge.

Chinkyoo Kim, D.A. Walko, I.K. Robinson (University of Illinois at Urbana-Champaign)

Many metals form $\sqrt{3}\times\sqrt{3}$ structures when evaporated onto Si(111). However, the column-V metal As has been shown to produce a (1x1) structure by simply replacing the first layer of Si atoms. Since Sb is also in column-V, it might be expected to show the same structure on Si(111) as that induced by As. STM and other studies have shown the evidence that Sb gives a clear $\sqrt{3}\times\sqrt{3}$ structure instead.

In this experiment, we measured fractional order in-plane peaks of the $\sqrt{3}\times\sqrt{3}$ -Sb/Si(111) to get Patterson function shown in Fig 1. The peaks in this function are predominantly Sb-Sb interatomic vectors in the structure. The 6 peaks are consistent with the "milk stool" trimer model shown in Fig 2, and are clearly inconsistent with the T_4 adatom structure seen for Al, Ga, In, Pb or with the trimer structure seen for Ag, Au.

Figure 1. Patterson function of $\sqrt{3}\times\sqrt{3}$ -Sb/Si(111)

Figure 2. Milk stool trimer model of $\sqrt{3}\times\sqrt{3}$ -Sb/Si(111)

D.A. Walko, K.L. Whiteaker, and I.K. Robinson (University of Illinois, Urbana)

The size and shape of submonolayer islands grown on crystalline surfaces are ultimately determined by the ability of adatoms to diffuse across the surface. We have studied the diffuse scattering from one-half monolayer (ML) of Cu on Cu(110) for various substrate temperatures and deposition rates. On this anisotropic surface, the islands will be needle-shaped, with the needles pointing in the $[1\bar{1}0]$ direction; the diffuse scattering is thus concentrated in the $[001]$ direction. Diffuse intensity was measured across a crystal truncation rod (CTR) at $q_{\perp} = 0.2 \text{ \AA}^{-1}$, approximately halfway between two Bragg peaks for maximum surface sensitivity.

Fig. 1 shows data (circles) for deposition rate 4.7×10^{-4} ML/s and substrate temperature 218 K. The solid line is an empirical fit to the data, namely, the CTR at $h = 0$ is modeled as a Gaussian and the diffuse scattering as a series of six Lorentzians centered at $\pm h_0$, $\pm 2h_0$, and $\pm 3h_0$. All Lorentzians have the same half-width; their height decreases with increasing $|h|$. The reciprocal of h_0 corresponds to the characteristic length scale of the islands (namely, the widths of the needles in units of atomic positions).

Fig. 2 plots the temperature dependence of the characteristic length $1/h_0$ (circles). Linear regression (solid line) determines a slope of 0.27 ± 0.01 eV. This slope is proportional to an activation energy of diffusion. Note that the data level off for $T < 213$ K, on the right side of the figure. Below this temperature, diffusion may be effectively frozen out. Evaluation of data for varying deposition rates and the relation to the activation energy of diffusion is in progress.

Figure 1. Transverse scan of Cu(110) CTR with 0.5 ML of Cu deposited at $T = 218$ K.

Figure 2. Arrhenius plot of fitting parameter h_0 . Each measurement corresponds to a separate deposition of 0.5 ML at a flux of $\approx 4 \times 10^{-4}$ ML/s.

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Development of local structure in sol-gel derived lead zirconate titanate thin layers *

X16C

D.L. Adler, S.S. Sengupta and D.A. Payne (Univ. of Illinois, Urbana)

EXAFS analysis was carried out to determine the evolution of local structure in lead zirconate titanate (PZT) thin layers prepared by a sol-gel technique. Earlier results obtained for partially heat-treated (below 500°C) bulk gels indicated the presence of separate Ti-O-Ti, Zr-O-Zr and Pb-O-Pb networks.

In the present study, thin layers of were spin-coated on polycrystalline alumina substrates and initially heat-treated to 300°C to remove organics. The amorphous coatings were then sequentially heat-treated to various temperatures between 400-625°C for EXAFS analysis. As expected, the first nearest neighbor for all metal cations was oxygen. For lead titanate (PT), a clear and definite change in second shell coordination was evident upon heat-treatment: between 450°C and 500°C, the cation distribution in the second shell of Ti changed abruptly from nearly all Ti to mostly Pb, with a corresponding increase in the bond distance. Evolution to A-O-B type bonding, representative of the basic perovskite building block, was complete by 550°C. The third shell, however, showed a lack of order even at 550°C, suggesting that the characteristic long-range order of the crystalline phase had not fully developed, and required further heat treatment. Fig. 1 compares the magnitudes of the Fourier transform for experimental Ti K-edge data at two different temperatures, with previously obtained results for amorphous bulk gels (heat-treated at 375°C) and crystalline PT. In contrast to PT, the PZT70/30 and lead zirconate (PZ) specimens did not show a sharp change in second neighbor coordination during heat treatment up to 625°C. Further analysis is in progress.

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Superstructure peaks in lead magnesium niobate (PMN)

X16C

D. Fanning, D. Adler, I. Robinson (U. of Illinois)

A single crystal sample of lead magnesium niobate (PMN) was studied on the X16C beamline. PMN is a ferroelectric "relaxor," exhibiting a broad ferroelectric to paraelectric phase transition near room temperature. Relaxors are also characterized by their high dielectric constants and frequency dependent behavior. PMN has the general perovskite structure ($a=4.04$ Å) with Pb on the corner, 3 O atoms on the faces and a random distribution of Mg and Nb ions (in a 2:1 ratio) on the body centered site.

The sample was found to have well formed superstructure peaks of type $(h+1/2, k+1/2, l+1/2)$ (h, k, l integers) which had widths on the order of 0.01 Å $^{-1}$ indicating a domain size around 100 Å. Electron diffraction experiments have shown that this domain size is not affected by annealing or preparation technique. Hence, it is not certain whether these domains are related to PMN's ferroelectric behavior.

Radial scans were made through many half-order peaks, and their integrated intensities were calculated. Figure 1 is a plot of $|F|$ vs. $|q|$ for superstructure reflections of one set of data at room temperature.

Superstructure reflections of the type $(h+1/2, k+1/2, l+1/2)$

Figure 1.

Equation of State on MgAl_2O_4 Spinel
G. L. Chen, J. I. Ando, Y. B. Wang, and D. J. Weidner (CHIPR, USB)

Magnesium aluminate spinel MgAl_2O_4 is an analogue member of the spinel phase of $(\text{Mg,Fe})_2\text{SiO}_4$ which is one of the major constituents of the 400-670 km transition zone of the Earth's mantle.

The thermoelastic properties of the spinel family are of particular importance in understanding the mineral physics of the transition zone region. Ultrasonic measurements on the MgAl_2O_4 spinel suggested that there is a pronounced curvature in the bulk modulus at pressures around 10 GPa at ambient conditions.

We have, using synchrotron x-radiation, determined the cell volumes of the cubic MgAl_2O_4 spinel to a pressure of ~ 10 GPa and a temperature of 1200°C. Seven P-T cycles were used to cover the P-T space of the measurements. The measurements were taken along the isotherms (1200°C, 1000°C, 800°C, 600°C, 400°C, 200°C, and 35°C - ambient temperature). The temperature was controlled to within two degrees during the measurements. The high-temperature form of the Birch-Murnaghan equation of state (EOS) was used to fit the complete data set.

While the majority of the data can be fit well, there are deviations of the ambient temperature data at low pressures from the fit. More intriguingly, the ambient cell volume measured before the experiment is lower than the calculated volume at the ambient conditions. Unfortunately, the ambient cell volume was not measured upon the completion of the run and therefore, we do not have information on whether the sample has been irreversibly altered during the P-T runs. TEM work is underway to provide clues to this question.

The results of the Birch-Murnaghan EOS fit are: $V_0 = 528 \text{ \AA}^3$; $K_0 = 182 \text{ GPa}$; $\frac{dP}{dK_0} = -0.0257 \text{ GPa/K}$; $a_0 = 1.77 \times 10^{-6} \text{ K}^{-1}$; $\frac{d^2P}{dK_0^2} = 1.18 \times 10^{-8} \text{ K}^{-2}$.

Figure 1. Unit cell volume of MgAl_2O_4 spinel as a function of pressure for several temperatures. Line is the fit to data using the high temperature Birch-Murnaghan equation of state, and the parameters listed above.

In-situ diffraction study of the cation distribution in the olivine solid solution of Ni_2SiO_4 and Mg_2SiO_4 at high pressure
X17B1

J. H. Chen, R. Li, J. B. Parise, D. J. Weidner, Y. B. Wang, M. T. Vaughan, P. J. Schields (CHIPR, USB) and J. Kung (Australian National University)

While the temperature dependence of cation distribution in minerals has been a subject of study in recent decades, little is known of the pressure dependence of this phenomenon. However, the order/disorder state reflects the pressure-temperature conditions under which a mineral forms. The recently established high-pressure two-dimensional diffraction system at SARM85 at the X17B1 beamline allows the acquisition of quantitative diffraction data while maintaining the sample at high pressures and temperatures. We have begun to study the cation distribution of the olivine solid solution Ni_2SiO_4 and Mg_2SiO_4 with this diffraction system.

The structure of Ni-Mg olivine (Pbm) contains two different octahedral sites M1 and M2. The studies at high temperature and ambient pressure confirm the preference of Ni^{2+} to the smaller site, M1. The preference decreases with temperature.

The sample we used in this study is 1:1 Ni-Mg olivine which is synthesized by solid reaction at 1500°C and atmospheric pressure. The synthetic olivine was hot pressed to form a stress free chunk. Before loading in a high pressure cell, the sample was annealed at 800°C for 36 hours in an oven and then quenched by dropping into liquid nitrogen. Diffraction patterns were taken at two pressures (3 GPa and 4 GPa) and several temperatures (600°C to 1000°C in 100°C steps). Three patterns were taken at each P-T condition to investigate the kinetic effect of the cation distribution. Rietveld refinements were carried out with the diffraction data. Preliminary analysis shows the pressure effect is to increase the distribution coefficient K_d :

$$K_d = \frac{(N_2/Mg)_{M2}}{(N_2/Mg)_{M1}}$$

i.e. to order the cation distribution. The temperature effect under pressure is the same as that at room pressure, i.e. to decrease the distribution coefficient K_d . These investigations also show that the rate of cation redistribution between the M1 and M2 sites is very fast at high pressure and temperature.

Effect of Pressure on Cation Distributions in Nickel Aluminate Spinel (NiAl_2O_4)	X17B1
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J. H. Chen, J. B. Parise, D. J. Weidner, R. Li, Y. B. Wang and M. T. Vaughan (SUNY, Stony Brook)

The effect of pressure on cation distribution of Ni^{2+} and Al^{3+} in nickel aluminate spinel (NiAl_2O_4) has been studied by *in-situ* high-pressure x-ray diffraction with SAM85 at the X-17B1 beamline with a recently established two dimensional diffraction system¹.

The cation distribution in NiAl_2O_4 spinel is expressed by:

$(\text{Ni}_{1-x}\text{Al}_x)^{[4]}(\text{Ni}_x\text{Al}_{2-x})^{[6]}\text{O}_4$ where [4] and [6] represent the tetrahedral and octahedral sites, and x represents the degree of inversion. The diffraction patterns of NiAl_2O_4 spinel were taken at room pressure and at 7.6 GPa after quenching from 800°C. Structure refinement shows that the x value increases from 0.857 at room pressure to 0.914 at 7.6 GPa. The cation distribution of Ni^{2+} and Al^{3+} tends to more ordered (inverse) under pressure.

The effect of pressure or temperature on the cation distribution in spinel is mainly dependent on a characteristic volume ΔV ($V_{\text{inverse}} - V_{\text{normal}}$). If ΔV is positive, the cation distribution tends to more disordered for inverse spinel and ordered for normal spinel under pressure. If ΔV is negative, the cation distribution tends to more ordered for inverse spinel and disordered for normal spinel under pressure. Temperature gives the reverse effect: NiAl_2O_4 spinel has a negative ΔV and the x value of NiAl_2O_4 spinel tends to decrease when the temperature is increased.^{2,3}

References:

¹Jiuhua Chen, Donald J. Weidner, Michael T. Vaughan, John B. Parise and Rui Li, AGU 1995 Spring Meeting (M32A-09).

²Robert Hazen and Alex Navrotsky, Am. Min. to be published.

³Jeanette Roelofsen, *et al.*, Am. Min. 77, 522 (1992).

Quantitative x-ray diffraction with an imaging plate at high pressure and temperature	X17B1
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J. H. Chen, D. J. Weidner, M. T. Vaughan, R. Li, J. B. Parise, and Y. B. Wang (Center for High Pressure Research, University at Stony Brook)

Crystal structure determinations of high pressure phases of minerals and structure refinements of minerals as a function of pressure and temperature require quantitative measurements of diffraction peak intensities. Energy dispersive diffraction (EDD) methods are widely applied to a large volume press for experimental convenience. However, with these methods it is difficult to derive reliable diffraction intensities due to uncertainty in the spectrum of the incident radiation and difficulty in making precise corrections for absorption by the pressure medium and other surrounding materials. To get quantitative diffraction data, angle dispersive diffraction (ADD) using monochromatic radiation is more reliable. At the X17B1 beamline, the Stony Brook group has set up an EDD system with the large volume press SAM85. With this apparatus, we have established an ADD system with a highly sensitive area detector imaging plate (IP). A Laue-Bragg monochromator is adopted in the system and the radiation can be easily switched between white and monochromatic mode by moving the beam stop at the downstream side of the monochromator. Orientation of the IP is aligned by taking full Debye rings on the plate, and the inclination is corrected by the relation

$$Y_1 = \frac{f}{L} Y_2^2 + d$$

where f is the inclination angle, d the center offset, $Y_1 = \frac{x_+ - x_-}{2}$ and $Y_2 = \frac{x_+ + x_-}{2}$. A double cassette holder is adopted. Sample-to-IP distance is derived from the double exposures. Diffraction intensities are obtained by integrating the diffraction arcs recorded on the IP. The observed data are processed by the General Structure Analysis System (GSAS) program for the structure refinement. Quantitative diffraction data on NiAl_2O_4 spinel and the olivine solid solution of Ni_2SiO_4 and Mg_2SiO_4 have been collected at high pressure and temperature to study the cation distribution in the crystals as function of pressure and temperature.

AgI/Ag ₂ SeO ₄ : a glassy and crystalline fast ion conductor. Determination whether AgI containing glasses have a biphasic structure	X17B1
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C. Cramer, D.L. Price, M.-L. Sabounji (ANL), and S.W. Martin (Iowa State University)

AgI-containing glasses are fast ion conductors showing tremendous dc conductivities reaching values of about $10^{-2} \Omega^{-1} \text{cm}^{-1}$ at room temperature. So far, a lot of work has been done to link the high ionic conductivity to structural features of these glasses. A crucial question is how the AgI enters the glass network. There has been debate whether or not this sort of glasses contain a biphasic structure forming AgI rich regions within the glassy matrix. Whereas normal x-ray and neutron diffraction techniques just yield the total structure factor including all kinds of correlations, anomalous x-ray diffraction (AXD) can determine structure factors due to specific elements.

On X17B1 we performed AXD experiments on two sorts of AgI containing glasses ($x\text{AgI} \cdot (1-x)\text{Ag}_2\text{SeO}_4$ and $x\text{AgI} \cdot (1-x)\text{AgPO}_3$) of various compositions, looking at the K-absorption edges of Ag and I. The investigated Q -range covered $0.5 \text{ \AA}^{-1}$ to $15 \text{ \AA}^{-1}$. Especially, we obtained the differential structure factors $\Delta S_{\text{Ag}}(Q)$ and $\Delta S_{\text{I}}(Q)$ of $0.4\text{AgI} \cdot 0.6\text{AgPO}_3$ from diffraction data taken near and far beyond the silver (25.486 keV, 25.224 keV) and the iodine K-absorption edges (33.313 keV, 32.836 keV).

Based on Reverse Monte Carlo Simulations Börjesson et al. [1,2] have calculated partial structure factors for an AgI phosphate glass of similar composition. It turns out that the differential structure factors we get can be constructed by superimposing Börjesson et al.'s calculated partial structure factors of the relevant elements. The differential structure factor $\Delta S_{\text{Ag}}(Q)$ is strongly dominated by Ag-Ag and Ag-I correlations (the weight of Ag-P and Ag-O correlations are much smaller). By comparing our data with Börjesson et al.'s results, we can conclude that a minimum at about $0.7 \text{ \AA}^{-1}$ is due to Ag-I correlations, a maximum at about $1 \text{ \AA}^{-1}$ and a minimum at about $2 \text{ \AA}^{-1}$ are due to both Ag-Ag and Ag-I correlations. For the differential structure factor $\Delta S_{\text{I}}(Q)$ we find that a minimum at $1 \text{ \AA}^{-1}$ is due to I-P and I-O correlations and a maximum at $2 \text{ \AA}^{-1}$ to I-P and I-I correlations. These results can be taken as experimental confirmation of Börjesson et al.'s computer simulations, indicating that – although there might be conducting pathways of AgI – there is no hint of the formation of so-called "AgI clusters" or "AgI microdomains" with a crystal like structure.

[1] L. Börjesson, W.S. Howells, Solid State Ionics 40/41, 702 (1990)

[2] L. Börjesson, R.L. Mc. Greevy, J. Wicks, Journal de Physique III, Vol. 22, gt C2-109(1992)

X-ray microbeam pseudotherapy vs. therapy using two cross-fired arrays through normal vs. tumor-bearing rat brains *	X17B1
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Microplanar (microbeam) radiation therapy (MRT) [1] research with the X17B1 beam filtered through 0.25 mm Gd has shown a substantial tissue-sparing effect to 1250 Gy when rat brains are irradiated unidirectionally in many (≤ 100) parallel slices, each $\leq 47 \mu\text{m}$ wide and $\leq 12 \text{ mm}$ high, with 75-200 μm spacing on center [2,3]. It is postulated that this effect is from the survival of endothelial and, perhaps, other cells between individual slices, which later divide and replace lethally irradiated cells. This enables MRT when a target is crossfired. In a pseudotherapy experiment matching a therapy experiment [3], Fischer 344 rats were irradiated prone with right anteroposterior and lateral arrays at entrance absorbed doses of 625 Gy or 312 Gy; the slices were 27 μm wide and 12 mm high; each array had 100 slices, 100 μm on center. In the therapy experiment [3], similar rats with $\approx 40 \text{ mg}$, imminently ($\approx 7 \text{ d}$) lethal, right intrastriatal 9L gliosarcomas were irradiated 14 days after tumor initiation.

There were eight rats in each of the 625- and 312-Gy pseudotherapy groups. Fig. 1 shows the survival histograms of the former and those of similar therapy groups. All 312-Gy normal rats survived $> 60 \text{ d}$. Necropsies show that, although tumor (if any) and brain tissues are ablated in most 625 Gy-crossfired rats, those tissues are ablated only in $\approx 1/2$ of 312 Gy-crossfired rats. Crossfiring with 625 Gy leads to longer survivals of tumor-bearing than of normal rats, perhaps because the tumor shifts vital midline structures leftward. The reverse survival pattern is observed after the 312 Gy irradiations, apparently because of $\approx 50\%$ failure in tumor control.

[1] D.N. Slatkin, P. Spanne, F.A. Dilmanian, and M. Sandborg, Med. Phys. 19, 1395-1400, 1992.

[2] D.N. Slatkin, P. Spanne, F.A. Dilmanian, J.-O. Gebbers, and J.A. Laissue, Proc. Natl. Acad. Sci. USA 92, 8783-8787, 1995.

[3] D.N. Slatkin, F.A. Dilmanian, M.M. Nawrocky, P. Spanne, J.-O. Gebbers, D.W. Archer, and J.A. Laissue, Rev. Sci. Instrum. 65, 1495-1460, 1995.

Figure 1. Survival histograms, irradiation on day 0: a) unirradiated, tumor; b) 625 Gy, normal; c) 312 Gy, tumor; d) 625 Gy, tumor.

* We thank N.F. Gmür, M. Kershaw and B. Ren for assistance. Research supported by the Office of Health and Environmental Research, U.S. DOE.

Simultaneous Resistivity and *In-situ* X-ray Determination of Phase Transitions in Bismuth in a Multi Anvil Apparatus *

I. M. Fiesch, J. E. Uris, G. D. Gwanmesia, and R. C. Liebermann (CHPR, University at Stony Brook)

Pilot experiments were conducted to determine the optimum pressure-time path for detecting transitions in bismuth up to pressures of 8 GPa using resistivity measurements in conjunction with x-ray determinations of cell pressure. All experiments were performed in a DIA-type, cubic anvil high-pressure apparatus (SAM-85) at room temperature.

Phase transitions were detected from changes in the resistance of the bismuth, and pressure was determined using NaCl as a standard according to the Decker scale. The cell assembly consists of two half-cubes of boron-epoxy; inside each half-cube is a cylindrical hole filled with a layer of AgCl on the top of a layer of NaCl and polyethylene (2:1 weight ratio). The thin (100 micrometers) bismuth wire is placed in the middle of the sandwich produced by the two half-cubes and connected to the constant current (10 mA) power source via platinum strips. The polyethylene serves to minimize the deviatoric stress in the NaCl layer during compression at room temperature.

Figure 1. Cell assembly used in bismuth calibration experiments.

* This work was supported by the National Science Foundation under a grant to the Center for High Pressure Research

In situ high-pressure X-ray diffraction study of FeSi

F. Guyot (IPGP, Paris), J. Zhang (CHPR, USB), I. Martinez (ENS Lyon, France)

Silicon has been proposed to be an important alloying element in the outer core of the Earth. In order to discuss the possibility of silicon incorporation during the formation of the core, high-pressure high-temperature properties of iron-silicon alloys are needed.

In this study, we measured the molar volumes of synthetic iron silicide FeSi *in situ* at high pressure and temperature in the DIA type multi-anvil apparatus (SAM85) installed at the superconducting wigglers X17B beamline. The samples were studied at high pressure and temperature in the cell were evaluated from the NaCl couple, and nonhydrostatic stress components in the cell were evaluated from the spectra taken on cooling. We used the method of Weidner *et al.* (1992). Deviatoric stresses were annealed out by heating samples at temperatures exceeding 1000 K. Then, in this study, special attention has been paid to collect a sufficient number of data points on each isotherm (20 at 300 K, 8 at 673 K, 873 K, and 1073 K).

The following parameters have been obtained by fitting on a second order Birch-Murnaghan equation of state: $K_0 = 172(3)$ GPa; $\frac{dK}{dP} = -0.0043(8)$ GPa/K; and $\alpha = 5.1(4) \times 10^{-5}$ K⁻¹ (average value between 300 K and 1100 K). These parameters are now in the process of being included in models of the formation of the Earth in order to estimate the silicon content in the core corresponding to the various differentiation schemes proposed.

Reference: D. J. Weidner, M. T. Vaughan, and Y. B. Wang, in *High Pressure Research*, ed. by Syono and Manghnan, TERRAPUB/AGU, pp 13-17, 1992

Equation of state of stishovite

X17B1

J. Liu, G. Chen, and R. C. Liebermann (CHiPR and USB)

Stishovite, a high-pressure polymorph of silica with the rutile structure, has been the subject of much research because it is a candidate component for the mantle of the earth. As such, its elastic and thermodynamic properties are important for interpretations of seismic observations and for modelling the phase equilibria in stishovite-bearing phase assemblages at high pressures and temperatures. Previous acoustic studies have constrained the bulk modulus K_0 and its pressure derivative K'_0 . However, little is known about its equations of state at simultaneous high pressure and temperature.

The purpose of this study is to determine the $P-V-T$ behavior of stishovite within its $P-T$ stability field using a DIA-type, cubic-anvil apparatus (SAM 85) and *in situ* x-ray diffraction techniques on the X17B superconducting wiggler beamline at NSLS. In this beam time, we successfully obtained $P-V-T$ data for stishovite in the temperature range from 30°C to 1100°C and pressures from 1 bar to 11 GPa. Analyses of the data show that pressure environment of the sample during the experiment is near hydrostatic (deviatoric stress was lower than 0.4 Kbar at all pressures and temperatures).

We are currently modelling these data to determine the temperature derivative of the bulk modulus.

Characterizing the unit-cell volume of talc as a function of pressure and temperature *

X17B1

P. J. Schields (CHiPR, USB), K. Bose (CHiPR, Princeton), Y. B. Wang, and D. J. Weidner, (CHiPR, USB)

To determine the equation of state and the behavior of planer disorder in talc, EDXRD at high temperature and pressure was done using a DIA-type cubic-anvil press (SAM-85).

Disorder reduces the intensity of many Bragg lines, and therefore the remaining lines could only be indexed as monoclinic. The unit-cell volume is shown in Fig. 1. The room-temperature volumes were fit to the Birch-Murnaghan equation of state to derive the compressibility values of: $K = 32.6(3)$ GPa and $K' = 13.8(4)$.

Fig. 1. Talc volume vs. pressure.

Figure 1. Unit cell volume of talc as a function of pressure at temperatures ranging from 300 K to 1025 K.

* This work was supported by the NSF under a grant to the Center for High Pressure Research.

Exploring the stress-induced transformation of FCC TiC to the 8H HCP polytype using high pressure and high temperature	X17B1
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P.J. Schields (CHiPR, USB)

We have attempted to reproduce a recently discovered [1] stress-induced polytypic transformation of the FCC NaCl-type structure of TiC to the HCP 8H polytype. We increased pressure to 8.8 GPa to generate nonhydrostatic stresses, but did not detect a phase change. Heating to 1473 K, and further pressure treatments did not induce a phase transformation.

1. Chien, F., R.J. Clifton and S.R. Nutt, Stress-induced phase transformation in single crystal titanium carbide, *J. Am. Cer. Soc.*, 78 [6], June (1995).

Equation of State of $\text{Ca}(\text{Ti},\text{Si})\text{O}_3$ Perovskite	X17B1
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Y. Sinenikov, J. Kung, and Y. B. Wang (CHiPR and USB)

$\text{Ca}(\text{Ti},\text{Si})\text{O}_3$ and CaTiO_3 solid solution perovskites have been the subject of the present study to constrain the properties of unquenchable CaSiO_3 perovskite through the elasticity systematics in the system CaSiO_3 - CaTiO_3 . There are numerous studies on the elasticity of CaTiO_3 perovskite (perovskite *sensu strictu*), which is stable at room pressure and temperature. However, little is known about its equation of state at simultaneous high P and T, and nothing about the properties of the solid solution perovskites $\text{Ca}(\text{Ti},\text{Si})\text{O}_3$.

Such intermediate compound have been synthesized in the Stony Brook High Pressure Laboratory using the multianvil apparatus USSA-2000. The $P-V-T$ behavior of two samples has been studied within their P-T stability field using a DIA-type, cubic-anvil apparatus (SAM 85) and *in situ* x-ray diffraction techniques on the X17B superconducting wiggler beamline at NSLS. In this beam time, we successfully obtained $P-V-T$ data for CaTiO_3 and $\text{Ca}(\text{Si},\text{Ti})\text{O}_3$ in the temperature range from 30°C to 900°C and pressure from 1 bar to 10 GPa. Analyses of the data showed that pressure environment of the sample during the experiment was nearly hydrostatic. The whole dataset is currently being minimized in full in order to obtain all the thermoelastic parameters simultaneously.

Preliminary results [$K_0=165$ GPa for CaTiO_3 and 184 GPa for $\text{Ca}(\text{Ti},\text{Si})\text{O}_3$] yield a trend of increasing bulk moduli toward Si rich compounds, which is consistent with the ultrasonic measurements on the same materials.

Y. B. Wang, D. J. Weidner, J. Z. Zhang, I. Martinez, Y. J. Wu, G. L. Chen, Y. Sinelnikov, M. T. Vaughan, R. C. Liebermann, (CHiPR, USB) and G. D. Gwanmesia (Delaware SU)

Pressure-volume-temperature ($P-V-T$) relations of garnets along the pyrope (Py) - majorite (Mj) join have been experimentally determined up to 11 GPa and 1073 K with SAM-85. Well-sintered, polycrystalline samples, with compositions $\text{Py}_{62}\text{Mj}_{38}$ and $\text{Py}_{20}\text{Mj}_{80}$, respectively, were previously synthesized in a 2000-ton uniaxial split-sphere apparatus (USSA-2000) recovered with controlled $P-T$ paths in order to minimize residual internal stresses.

The equation-of-state experiments were carried out with samples embedded in NaCl, which was used as the pressure standard as well as to provide a quasi hydrostatic environment at high temperatures. For each $P-V-T$ measurement, non-hydrostatic stress components in the samples were evaluated from the NaCl spectra, following the method given in (1). These stresses were relaxed at above 1000 K, and the spectra collected on cooling were the least contaminated. Only such hydrostatic spectra were used to extract quantitative equation-of-state data. As the materials were metastable, the $P-V-T$ data were collected under the conditions where the behavior was reversible (up to 1073 K).

A new anvil geometry design has greatly enhanced the capability of varying pressure during one single experiment, allowing a complete coverage in pressure along several isotherms at 1073, 873, 673, 473 and 300 K, respectively. These $P-V-T$ data allowed extraction of isothermal, isobaric, as well as isochoric properties. [Ref: (1) Weidner *et al*, High Pressure Research, Geophys. Monogr. 67, pp 13-17, 1992.

$$K_{T0} = 162(3) \text{ GPa}$$

$$K'_{T0} = 4.4(5)$$

$$V_0 = 909.05(12) \text{ cm}^3 / \text{mol}$$

$$\left(\frac{\partial K_T}{\partial T} \right)_V = -0.0037(11) \text{ GPa} / \text{K}$$

$$\left(\frac{\partial K_T}{\partial T} \right)_P = -0.0 - 21(2) \text{ GPa} / \text{K}$$

$$\alpha_0 = 1.946(65) \times 10^{-8} \text{ K}^{-1}$$

Figure 1. Thermoelastic parameters extracted from the data. α_0 is the pressure thermal expansion.

Figure 2. $P-V-T$ data for $\text{Py}_{62}\text{Mj}_{38}$. Solid circles room temperature data that are contaminated by non-hydrostatic stress (and thus are not used in equation of state fit). Open circles quasi-hydrostatic data; curves result of fit using the high-temperature Birch-Murnaghan equation of state (from bottom up, temperatures are 300, 473, 673, 873, and 1073 K, respectively).

D. J. Weidner, J. H. Chen and Y. B. Wang (CHiPR, USB)

$(\text{Mg,Fe})_2\text{SiO}_4$ olivine (α phase) is the most abundant mineral in the upper mantle. Under pressure and temperature, the $(\text{Mg,Fe})_2\text{SiO}_4$ olivine undergoes a phase transformation to the modified spinel (β) phase, then to the spinel (γ) phase, and then some higher pressure phases. The $\alpha-\beta-\gamma$ phase transformations are believed to result in the discontinuities of seismic wave velocity at 400 and 520 km depth of the earth's transition zone. These phase transformations are strongly dependent on composition (Mg/Fe ratio) as well as pressure and temperature. There are continuous investigations on the $\alpha-\beta-\gamma$ phase transformations, and the topology of the phase diagram is well known. However, there are still some questions concerning details of the phase diagram such as the composition of the coexisting α , β and γ phases on the univariant boundary and the phase equilibrium for the system $\text{Mg}_2\text{SiO}_4 - \text{Fe}_2\text{SiO}_4$.

Aiming to investigate these questions, we have carried out *in-situ* diffraction studies on the $(\text{Mg,Fe})_2\text{SiO}_4$ system at the X17B1 beamline. Double-sample assemblies are used in each run. Starting materials have different composition, $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ and $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$. The pressure and temperature are increased up to 14 GPa and 1300°C, and cross and recross the univariant boundary. Energy diffraction patterns are taken at different $P-T$ conditions near the univariant boundary. A series patterns are also taken as a function of time while the pressure and temperature are held constant. In Run No. ABG23, we found that β phase is present at 12 GPa and 1000°C and is not present at 12 GPa and 1100°C, which locates the univariant boundary.

The structure refinement program GSAS is applied to analyze the energy dispersive data. A good Rietveld analysis can be obtained by fitting the incident spectrum first (Figure 1). Messages of phase fractions and atomic occupation fractions come out from the analysis while the atomic positions are fixed. The data analysis is still under progress.

Figure 1. An example of Rietveld fitting for the energy dispersive diffraction patterns of $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ at high pressure.

Studying Rheology Under Mantle Pressure and Temperature Conditions *

X17B1

D. J. Weidner, Y. B. Wang, G. L. Chen, and J. I. Ando (CHiPR, USB)

Measurement of rheological properties of Earth materials in a multi-anvil devices is accomplished with the aid of a synchrotron generated X-ray probe. Deviatoric stresses are generated by compressing a polycrystalline powder as a result of the interaction between individual grains. The stress is quantified by measurement of the broadening of the diffraction peaks. Generally, the magnitude of the deviatoric stress will exceed the nominal pressure unless the sample fails or flows. The change of the peak width with time defines the strain rate of the sample. Taken together, these data provide constraints on the rheological properties for these conditions.

In situ X-ray diffraction measurements of MgAl_2O_4 spinel under 10 GPa confining pressure and temperatures up to 1100°C provide an example of such data. Strain rates of the order of 10^{-8} s^{-1} were measured at 600°C with deviatoric stresses of the order of a few GPa, over a duration of four days. The total plastic strain in the sample amounted to a few per cent.

The observed stress-strain-rate-temperature relations quantitatively agree with those for the spinel given by Frost and Ashby *Deformation-Mechanism Maps The Plasticity and Creep of Metals and Ceramics, 1984* and correspond to the plasticity-power law creep boundary for this material. The current limits of this approach are defined by the resolution of X-ray energy.

Future improvements will come using monochromatic sources with high resolution detection systems. This will enable lower stress determinations and hence higher temperatures.

Figure 1. Strain in MgAl_2O_4 spinel and $\text{Py}_{50}\text{Mj}_{50}$ garnet at 10 GPa and 600°C over a period of four days.

* This work was supported by the NSF under a grant to the Center for High Pressure Research

T-Cup: A New High-Pressure Apparatus for X-Ray Studies

X17B1

D. J. Weidner, Y. B. Wang, M. T. Vaughan, C. C. Koleda (CHiPR and USB) and I. C. Getting (CHiPR and U Colorado at Boulder)

We have designed and tested a new apparatus for *in-situ* X-ray diffraction studies under high pressures and temperatures. The apparatus is a two-stage system; the first stage is a steel cylinder split into six parts and fastened onto the upper and lower guide blocks, enclosing a cubic cavity (19.5 mm edge length and the [111] axis of the cube stays vertical) which contains the second stage anvil assembly. The hydraulic press used for SAM-85 DIA guideblocks is used to apply up to 200 ton load. The second stage is assembled outside the press and consists of eight WC cubes each with 10 mm edge length separated by spacers. Each cube has one corner truncated into a triangular face; the eight truncations form an octahedral cavity in which the pressure medium is compressed.

The cell assembly is an octahedron made of semi-sintered MgO or boron-epoxy. Incident x-ray beam passes through the gaps between WC cubes in the [110] direction of the eight-cube assembly and diffracts off parallel to one of the (100) planes, through gaps between the WC anvils, with a diffraction vector 35.3° from the vertical plane. A special holder is built for a solid-state detector for energy dispersive mode at several 2θ angles. We compressed NaCl at room temperature to 160 ton force and generated 18+ GPa pressure. Decker's equation of state for NaCl was used to determined pressures in the cell assembly.

Figure 1. Results using Toshiba F-grade WC cubes with various truncation sizes, pressure media, gasket systems, and taper angles near the truncation. Light gray line show results using Kenametal carbide cubes.

The Time-resolved X-ray Strength Study of Two Garnet Powder Samples *	X17B1
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Y. Wu, Y. Wang, J. Ando, D. J. Weidner, and M. T. Vaughan (CHiPR, USB)

The time dependence of microscopic deviatoric stress can provide a direct measurement on the viscosity of minerals at high pressure and temperature. Using a DIA-type cubic anvil apparatus (SAM-85) at the X17B1 beam line, we studied this problem on two powdered garnet samples with different composition. One is the pure pyrope (Py₁₀₀), another is 50% pyrope and 50% majorite (Py₅₀Mj₅₀). The two samples were simultaneously compressed (in different parts of the same chamber) to 9 GPa at room temperature, and then heated to 675°C, finally heated to 860°C. Using the method developed by Weidner^(1,2,3), We analyzed the microscopic strain from peaking broadening for the (400) and (420) diffraction lines. During the increase of the pressure at room temperature, we observed the microscopic strains of the two garnets both became almost constant after 5 GPa, which is an indication of the samples' strains have reached their yield point. Continuing increasing the pressure after the yield point, the strain values of these two garnets are becoming nearly the same. Keeping the pressure at 9 GPa and temperature at 675°C, we studied the relaxation process with time of the two garnets by observing the changes in the diffraction peak width. The microscopic strain of Py₅₀Mj₅₀ decreased monotonically with time, first very fast, then became much slower (Figure). The microscopic strain of Py₁₀₀ almost immediately decreased to zero. When the temperature was further raised to 860°C, the microscopic strain of the majorite rich garnet (Py₅₀Mj₅₀) continued to weaken. From this experiment, we conclude that Py₅₀Mj₅₀ is much stronger than pure pyrope (Py₁₀₀) at high pressure and high temperature. The microscopic strains of the two garnets show quite different temperature dependence at high temperature and pressure although their yield points at room temperature are nearly the same. Thus the composition of garnet has a great influence on its mechanical properties. Further studies on the viscosity of garnets from the time-resolved relaxation process are being carried out.

References ¹ D.J. Weidner, Y. Wang, NSLS Annual Report, 1993; ² D.J. Weidner, Y. Wang, M.T. Vaughan, Science, 266, p419-422, 1994; ³ D.J. Weidner, Y. Wang, M.T. Vaughan, Geophys. Res. Lett., 21, 753-756, 1994

Figure 1. Strain in two garnets as a function of time. The filled symbols represent Py₅₀Mj₅₀ and the open symbols represent the pure pyrope. The diamonds are for the (400) line in both cases, and the squares are for the (420) line.

* This work was supported by the NSF under a grant to the Center for High Pressure Research

<i>In situ</i> X-ray diffraction studies of iron and iron silicide at high pressure and temperature *	X17B1
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J. Zhang (CHiPR, USB) and F. Guyot (IPGP, Paris)

Silicon has been proposed to be an important alloying element in the outer core of the Earth. Discussion of possible incorporation of silicon during the formation of the core needs high-pressure and high-temperature data on the Fe-Si alloys. In this study, we performed experiments on iron and iron silicide Fe_{0.91}Si_{0.09} up to 10 GPa and 1000°C, using a DIA-type, cubic-anvil apparatus (SAM85) in conjunction with *in situ* X-ray diffraction. The two samples were loaded in the same boron nitride capsule and separated by NaCl that also serves as pressure standard. Upon heating, the transition from bcc phase to fcc phase of iron was observed at 475±8 GPa, 525±7 GPa, 550±6 GPa, and 625±4 GPa. The transition from hcp phase to fcc phase of iron occurred at 500°C and 9 GPa. These results are consistent with previous *in situ* x-ray studies (e.g., Akimoto *et al.*, 1987). For Fe_{0.91}Si_{0.09}, the first appearance of fcc phase was observed at temperatures that are 250-300°C higher than that in pure iron at 7.5 and 9.5 GPa. At both pressures, however, the transition in Fe_{0.91}Si_{0.09} was sluggish and did not complete up to 1000°C. At 5 GPa and lower pressures, no fcc phase of Fe_{0.91}Si_{0.09} was observed at high temperature. Implication from these observations is that incorporation of Si in Fe strongly stabilizes the bcc structure. It is also proposed that the amount of Si that can be incorporated in fcc structure increases with pressure. During the cooling the reversibility of phase transformations in iron is kinetically controlled: at 7-8.5 GPa, the fcc phase was first transformed to the hcp phase at 300°C and then to the bcc phase at 100°C; at 5.5-7 GPa, however, the bcc phase first appeared at 400°C and the hcp phase then started growing at 200°C; at pressures below 4 GPa, the transition between the bcc phase and fcc phase of iron was reversible within 20°C.

The kinetics of the back transformation in iron is likely due to (1) metastability of hcp phase and (2) lower transition temperatures at high pressures because of the negative slope of the phase boundary.

Reference: Akimoto S., T. Suzuki, T. Yagi and O. Shimomura (1987), Phase diagram of iron determined by high-pressure/temperature X-ray diffraction using synchrotron radiation, *in* High Pressure Research in Mineral Physics, ed. by M. Manghnani and Y. Syono, pp. 149-154.

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P-V-T measurements of siderites at high pressure and high temperature *

X17B1

J. Zhang (CHiPR, USB) and I. Martinez (ENS Lyon, France)

It has been recognized that magnesite and siderite might be major reservoir for carbon in the Earth's mantle (*e.g.*, Katsura *et al.*, 1991; Li *et al.*, 1995). To understand the stabilities of carbonates, physical properties at high pressure and temperature are needed. We have continued to work on the P-V-T measurements of carbonates, using a DIA-type, cubic anvil apparatus (SAM-85) interfaced with *in situ* x-ray diffraction at the X-17B1 beam line. In this study, we used the natural siderite samples of compositions $(\text{Fe}_{.998}, \text{Mn}_{.002})\text{CO}_3$ and $(\text{Fe}_{.60}, \text{Mg}_{.38}, \text{Mn}_{.02})\text{CO}_3$ as the starting material.

Isothermal volume measurements were obtained at pressures and temperatures up to 9 GPa and 1273 K by the following procedures: (1) compression at room temperature to the maximum pressure, followed by heating to the desired temperature (usually 1073 K) and cooling to room temperature; (2) decompression to the next pressure of interest with repetition of heating and cooling cycles. From these measurements, the following physical parameters can be derived based on the Birch-Murnaghan equation of state and relevant thermodynamic relations: (1) bulk modulus at room temperature and its pressure and temperature derivatives; (2) thermal expansion as functions of pressure and temperature;

and (3) thermal pressures for a given volume. In combination with our previous work on magnesite MgCO_3 (Zhang *et al.*, 1995), it is also possible to examine variations in these physical properties with iron-magnesium substitution in carbonates.

References

Katsura T, Y Tsuchida, E Ito, T Yagi and W Utsumi (1991), Stability of magnesite under the lower mantle conditions, *Proc. Japan Acad.*, 67, 57-60.

Li X, J Nguyen, and R Jeanloz (1995), CO_2 and H_2O in the deep Earth: An experimental study using the laser-heated diamond cell, *Proc. of Conference on Deep Earth and Planetary Volatiles*, *in press*.

Zhang J, I Martinez, F Guyot, P Gillet, and SK Saxena (1995), *In situ* x-ray diffraction study on magnesite at high pressure and high temperature, *Phys. Chem. Minerals*, *submitted*.

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Synchrotron X-ray scattering study of the N-IC phase transition in Rb_2ZnCl_4

X17B1, X20C

M.P. Zinkin, R.A. Cowley (Oxford), D.F. McMorro (Riso), J.P. Hill (BNL)

Below $T_c \approx 303$ K, Rb_2ZnCl_4 undergoes a continuous phase transition from a normal crystalline (N) phase, to one-dimensionally modulated incommensurate (IC) phase characterized by a modulation wavevector q . The transition can be characterized by a two-component primary order parameter corresponding to the amplitude and phase of the modulation wave, the transition is expected to belong to the 3D-XY universality class. Higher harmonics of the modulation wave form a class of secondary order parameters for the transition.

Measurements of the temperature dependences of the intensities of the satellite peaks corresponding to the primary order parameter and the next two higher harmonics were performed on X20C. The resulting order parameter exponents are $\beta_1 = 0.35 \pm 0.01$, $\beta_2 = 0.87 \pm 0.01$, and $\beta_3 = 1.50 \pm 0.04$, in good agreement with recent theoretical predictions for the 3D-XY universality class.

Figures 1 and 2 show the critical scattering above T_c measured on X20C and X17B1 respectively. The second, sharp, component in the X20 data corresponds to critical fluctuations on length scale ~ 10 times those of the broad component visible in both data sets. The penetration depth of the 10 keV X-rays used on the X20 experiment was $\approx 20 \mu\text{m}$, whereas the 60 keV X17B1 experiment was performed in transmission, the ≈ 2 mm penetration depth being approximately equal to the sample thickness. This data is evidence for a near-surface origin of the second length scale scattering. The measured temperature dependence of the width of the broad component of the critical scattering results in a value of the inverse correlation length exponent $\nu = 0.66 \pm 0.02$, in agreement with the 3D-XY result.

Figure 1. Critical scattering measured on X20C. Note the presence of a second component in the scattering.

Figure 2. Critical scattering measured on X17.

K-edge Subtraction CT Imaging using the Angiography System *	X17B2
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A.M. Charvet (ESRF), F. Arfelli (NSLS/INFN), R. Menk (NSLS) and Z. Zhong (NSLS/SUNY)

1. Framework

We are interested in subtraction CT imaging of the human brain at the K-edge of iodine as a possible tool for in-vivo neurological studies of cerebral ischemia. Ischemia is the tissue damage resulting from a diminished blood supply. It is hoped that this technique will allow quantitative concentration measurements of contrast agents carried by the blood stream, such as iodine, giving access to blood volume measurements (a.k.a perfusion) in various areas of the brain.

The work reported here was intended as a preliminary evaluation of the suitability of the NSLS X17B2 angiography system for K-edge subtraction CT imaging of phantoms under dosimetry conditions comparable to that of a medical brain scanner. Potential problems included the vertical crossing angle of the two beams and dose rates differing by two orders of magnitude in angiography and CT.

2. Method and measurements

The angiography system simultaneously provides two monochromatic X-ray beams bracketing the iodine K-edge (33.17 keV). Both beams are about 5" wide and cross at the patient/sample position with a vertical angle between them of about 1 mrad. The intensity profile of both beams is measured simultaneously in a few milliseconds with a 600 element dual array silicon detector. Absolute intensity of the X-rays incident on the patient/sample is provided at the beamline, expressed in dose. For CT a rotation stage was used instead of the vertical translation used in angiography mode.

Various samples and phantoms were imaged to test the system, including an excised cow heart and a cow tail (with bone) with iodine-filled tubes inserted in them. In each case monochromatic CT images were obtained above and below the iodine K-edge, and the subtraction carried out. In addition, a dual energy subtraction image was obtained using 33 keV and 99 keV as the two energies by using the harmonics present in the X-ray beam.

Images of a 4" diameter plexiglass phantom with iodine-filled holes of dimensions 1/4", 1/8" and 3/32" were taken with iodine concentrations of 12 mg/cm³, 3.7 mg/cm³ and 0.082 mg/cm³. The images were reconstructed from 360 projections.

3. Results

Concentrations down to 0.082 mg/cm³ in 1/4" diameter details were visible in the reconstructed subtraction images. This is a very encouraging result since it can be further improved upon.

These preliminary measurements have shown that the Angiography system on X17B2 is well suited to take K-edge subtraction CT images of phantoms at the iodine K-edge. It will be possible to use it to determine the minimum iodine concentration which can be accurately measured on K-edge subtraction CT images under conditions (dosimetry in particular) scalable to an in-vivo brain CT scanner.

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Comparison of different detectors used in noninvasive coronary angiography with synchrotron radiation *	X17B2
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R.H. Menk, F.Arfelli, D.Chapman, N.Gmur, W.Thomlinson, Z.Zhong (NSLS)

At present, and in the near future, only the line scan geometry with synchrotron radiation used at the NSLS, HASYLAB and ESRF provides enough precision and time resolution to resolve the distal parts of the coronary arteries down to a size of 1 mm in diameter after a transvenous injection of the contrast agent. The limitations are of a technical nature and mainly due to the detector systems used in this application. During the last year we carried out measurements to compare the detector systems used at the NSLS X17B2 beamline and at the medical beamline at HASYLAB in Hamburg. At X17B2 we use a solid state Li drifted Si strip detector in current mode while at HASYLAB a multi-channel gaseous ionization chamber also driven in current mode is used. Both detector systems are able to resolve a coronary artery even in its distal parts down to a diameter of 1 mm if the photon flux behind the patient is high enough to satisfy the requirements of poisson statistics (20000 photons per pixel). For this flux the zero spatial frequency detective quantum efficiency (DQE) of both detector systems is comparable and about 0.6. For lower fluxes, however, the solid state detector has higher DQE values than the gaseous detector due to a noise level of about 10 photons (at 33 keV) in comparison to 88 photons, respectively. In both cases the noise level is dominated by the read out electronics. It should be pointed out that the intrinsic noise level of the gaseous detector itself is negligible. For both detectors the spatial frequency dependent DQE is similar with slight advantages for the gaseous detector. This is mainly due to a spatial resolution of 0.98 LP/mm (gas detector) instead of 0.8 LP/mm for the solid state detector. At the moment the dynamic range of both systems is limited by the read out electronics and a value of 32000 for the solid state detector and 43000 for the gaseous detector was found. The dynamic range of the electronics of the gaseous detector is nearly independent of the integration time (from 0.8ms to 400ms). In the case of the solid state detector the dynamic range is directly proportional to the integration time. The quantitative evaluation of the patient images taken so far shows that the average flux behind large iodine filled structures like the ventricles might differ from 2000 to 15000 photons per pixel depending on the physical conditions of the patient. Unfortunately one of the three arteries (circumflex) is normally hidden by these structures in all projections. In order to resolve the circumflex artery (2 mm in diameter filled with 10mg/ml iodine) with a signal-to-noise-ratio of three, 2000 photons per pixel are needed and in most of the cases this is obtained for reasonable skin entry doses (3-5rad per frame). At the same time the electronics' noise should be at least 3 times smaller than the associated poisson noise of 44 photons. Taking into account that the maximum number of photons behind the lung areas observed was 2640000 photons per pixel a dynamic range of at least 18 bits is required. That is two to three times more than the dynamic range of the present systems.

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Three-energy Coronary Angiography Imaging *

X17B2

W. Thomlinson, L.D. Chapman, N. Gmür and Z. Zhong (NSLS), R. Petr (Science Research Laboratory, Inc.)

The use of three monochromatic beams provides a technique of resolving the bone as well as improving iodine and soft tissue images taken with synchrotron beams. The standard two-energy image analysis uses an assumption that the bone and soft tissue absorption coefficients have the same energy dependence. Such is the case for our present program and artifacts are, in general, not a problem. However, this assumption can lead to significant image artifacts if the two energies are not within 200-300 eV of the contrast agent absorption edge. We are developing a compact radiation source which uses characteristic radiation lines as much as 2.5 keV apart.

At the NSLS, the angiography monochromator is a bent-Laue Si(111) crystal which produces the two primary beams about 130 eV above and below the iodine K-absorption edge. In addition, the third harmonic of these energies is also present at a level of about 0.4%. We were able to image an angiography pig heart phantom first with the two standard beams, and then with a single beam at the third harmonic. With proper calibration of the system, we then had two images near 33.17 keV and one at 99.9 keV. The subtracted three-energy images provided iodine, soft tissue and bone images of excellent quality. The analysis also provided a pixel map of the three components of the phantom. Using this information, it was then possible to generate images corresponding to those which would be obtained with any set of two or three-energy beams. The results demonstrate very clearly that for two energies more than a few hundred eV apart, the image quality rapidly degrades. This is important because the compact source images would contain significant artifacts unless a third energy image were to be obtained.

Monochromatic CT image sensitivity: results from preclinical multiple energy computed tomography [MECT]

X17B2

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Images from the monochromatic CT MECT, being developed for the human head and neck imaging, are presented. MECT is expected to be used for imaging the composition of carotid artery atherosclerotic plaque in terms of lipid/cholesterol, fibrous, and calcified tissues.

A Laue-Laue monochromator with two flat Si<111> crystals, and two CdWO₄-photodiode array detectors, one with 0.5 mm pitch and second with 1.84-mm pitch collimated to 0.92 mm elements (Analogic Corp.) were used. Images were acquired at 24° s⁻¹ rotation speed. The monochromator was detuned to 15-20% peak intensity at a fixed dose rate. For some images two separate 360°-data sets were collected with a 1/2 detector pitch lateral offset, then interlaced. Reference data were collected before and after each slice. The residual variations in the beam profile shape due to monochromator instabilities was 0.2% peak-to-peak.

Fig. 1 shows a standard "low-contrast" phantom insert, inside a 10.5 cm diam. acrylic cylinder imaged with MECT (left, high-res. det., no interlacing, 43 keV, 1.9 mm slice height) and with conventional CT (CCT, right, 80 kVp, 3 mm slice height), respectively. The phantom had 5 inserts of 8.0, 5.6, 4.0, 2.8, and 2.0 mm diam. and 0.6% contrast. Images had the same spatial resolution (≈ 6.5 lp/cm), an dose times slice height (≈ 6 cGy · mm). The image noise (S.D.) was ≈ 1.5 Hounsfield Unit (HU) for MECT and ≈ 3 HU for CCT. A 135-mm diam. acrylic cylinder containing 5 inserts of six 11-mm diam paraxial channels filled with iodine solutions of 240, 120, 60, 30, 15 and 0 μg I/cc was imaged with MECT (33.25 keV) and CCT (100 kVp, mean energy ≈ 45 keV). Fig. 2 shows CT numbers in one set of channels; the 240- μg -I/cc values are 26 HU for MECT and 13 HU for CCT. The MECT image noise was higher at 33.25 keV than at 43 keV, because 33.25 keV is not optimized for the size of the phantom.

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Figure 1.

Figure 2.

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Pressure-Volume/Temperature Data on Platinum
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X17C

Y. Cerenius, S. K. Saxena, P. Haggkvist (Institute of Earth Science, Uppsala University, Sweden)

A modified diamond-anvil cell as originally designed by Schifferl and others (Ming et al., 1987) was used to obtain the pressure-volume-temperature data on platinum. Gold was used as an internal standard for pressure measurement and for correcting the thermocouple determined temperatures. The cell was heated externally under a constant flow of argon. The sample was pressurized between diamonds of 450 micron culet size. In all, 46 pressure-volume-temperature data are available in the pressure range of 1 atm to 15 GPa over the temperature range of 300 to 900 K.

L. C. Ming, M. H. Manghnani, J. Balogh (1987) High-Pressure Research in Mineral Physics. TERRAPUB, Tokyo, 69-74.

Pressure-Volume Data on Platinum and Rhenium
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X17C

L. S. Dubrovinsky, S. K. Saxena, P. Haggkvist (Institute of Earth Sciences, Uppsala University, Sweden)

The available equations of state for platinum and rhenium are largely based on shock-wave data. Therefore, we considered it important to obtain pressure-volume data on these two metals, which are finding important application as standards in laser-heating experiments both as hot plates and for in-situ X-Ray studies. We pressurized Pt in a Mao-Bell cell with three different solid media: NaCl, MgO, and brucite $Mg(OH)_2$. Rhenium was pressurized with MgO and with Pt in two separate experiments. The highest pressure reached in these experiments was between 30 to 50 GPa. By combining the metals with the solids of different compressibilities, we hope to obtain not only the P-V data but also learn about the influence of different degrees of non-hydrostatic conditions on EoS.

High-Pressure Phase Transitions in LiVO_3 and $\alpha\text{-NaVO}_3$

X17C

Andrzej Grzechnik, Paul F. McMillan; Materials Research Group, Arizona State University

LiVO_3 and $\alpha\text{-NaVO}_3$ were studied in situ at high pressure in a diamond cell, using energy-dispersive X-ray diffraction at the X17C beam-line. Pressures were derived from the Au internal standard. The peak positions, unit cell parameters, and unit cell volumes were measured to 50 GPa.

LiVO_3 and $\alpha\text{-NaVO}_3$ have crystal structures related to the monoclinic silicate pyroxenes, $C2/c$. They are built up of corner-shared chains of the tetrahedral VO_4^{3-} units along [001], bound in a crystal network by the external cations at two non-equivalent sites, M1 and M2. Upon pressurizing, both compounds exhibit sluggish phase transitions from 3 to 5 GPa and from 4 to 6 GPa, respectively. Thereafter, the diffraction patterns showed no changes up to 50 GPa. The forms were identified by observation of the growth of the peaks corresponding to the phase with the six-fold coordinated vanadium cations as well as merging of the peaks for ambient pressure phases. A tentative unit cell for the high pressure phases for both compounds is based on the rhombohedral unit cell of LiNbO_3 . High pressure phase of LiVO_3 was non-quenchable, whereas the diffraction pattern for the quenched sample of NaVO_3 showed the presence of both ambient pressure and high pressure phases.

We propose a structural model for the high pressure displacive phase transitions in LiVO_3 and $\alpha\text{-NaVO}_3$. In this model, the observed sluggish forms involve breakdown of the chain pyroxene structure. The displacement of the oxygen atoms in the b-c plane (the $C2/c$ phases) causes the rotation of the tetrahedral and M2 octahedral chains. Eventually, this displacement is so large that the distances between the V cations and the oxygen anions in its second neighbor shell can be short enough for the V cations to change its coordination to six-fold. Such model is in accord with the information inferred from our high pressure infrared and Raman data for both compounds.

Iron at High Pressure and Temperature: The Stability of New Beta-Iron Phase

X17C

S. K. Saxena, L. S. Dubrovinsky, P. Haggkvist (Institute of Earth Science, Uppsala University, Sweden)

Spec pure iron powder sandwiched between layers of BaO was squeezed in Mao-Bell diamond anvil cell and heated with a Nd-YAG laser in CW mode at pressures between 40 and 60 GPa at Uppsala. The pressurized DAC's were taken to NSLS and the samples while still under pressure were studied at the beam line X17C. The new phase beta-iron with DHCP structure (Saxena et al., 1993, 1995) was found to be present on all heated spots at pressure up to 60 GPa. A detailed study of the available data is in progress and will provide us with a preliminary pressure-temperature phase relations of iron in its alpha, beta, gamma and epsilon polymorphs and some comparative information on their compressibilities at 300 K.

S. K. Saxena, G. Shen, P. Lazor (1993) Science, 260, 1312.

S. K. Saxena, L. S. Dubrovinsky, P. Haggkvist, Y. Cerenius, G. Shen, and H. K. Mao (1995) Science, 269, 1703.

Monitoring the Absorption of Deuterium into Palladium

X17C

E. F. Skelton, S. B. Qadri, P. L. Hagens, D. D. Dominguez (NRL), and J. Z. HU (CIW)

The Pd-H system is probably the most extensively investigated of all metal-hydrogen systems. Nevertheless, some of its properties at high (> 85%) hydrogen concentration still remain unexplained. The work recently performed on X17C represents the first in situ monitoring from microscopic volumes deep within a Pd-lattice as D is absorbed (or desorbed). Conventional x-ray sources, such as K-alpha radiation from a Cu tube, will only penetrate the first few microns of Pd. However, the high energy (> 80 keV) x-ray photons available on X17C, allow two orders of magnitude deeper penetration into the Pd. Moreover, because of the multiple order of magnitude increase in the synchrotron beam intensity, diffraction data can be obtained from extremely small volumes. For example, data were collected from a microspot only $18 \times 10^{-12} \text{ m}^3$ in volume. This spot could be located anywhere within a 1 mm diameter Pd wire. Using this, the alpha-beta transition induced in the Pd by the absorption (or desorption) of D was monitored from the outer edge to the core. Results show that, although the alpha-phase forms rapidly at both the surface and the core, there is considerable delay in the initiation of the beta-phase at the core, compared to that at the surface. Other features of the structural changes associated with the absorption of D into Pd have been observed. These details may lead to an improved understanding of this system, especially at high concentration levels, and could shed light on claims made for anomalous power production mechanisms in this system.

X-ray scattering studies of liquid crystalline polymer solutions under shear flow *

X18A

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Liquid crystalline polymers (LCPs) derive much of their technological utility as a result of the ability of flow fields encountered during processing to influence the molecular orientation state in the final product. We have used x-ray scattering as an in situ probe of molecular orientation in model LCP solutions [poly(benzyl glutamate) (PBG) in m-cresol, hydroxypropylcellulose (HPC) in water, and HPC in m-cresol], that are subjected to shearing flow in a rotating parallel disk flow cell. The flow cell consists of aluminum and steel disks that rotate relative to one another. Thin mica sheets are glued to the surface, and apertures are cut out of the plates to provide x-ray transmission. Image plates were used to collect two-dimensional scattering patterns. Exposure times could be made as short as a few seconds, enabling transient processes to be studied.

Figure 1 shows a typical scattering pattern, in which the flow direction is vertical. A double-lobed scattering pattern is observed, where the width of the peaks may be related to the degree of molecular orientation (through an orientation parameter, S). These solutions have also been studied at Northwestern University using flow birefringence as a probe of molecular orientation. We find excellent self-consistency between these two quantitative measures of molecular orientation. In all systems, molecular orientation is seen to increase with shear rate in steady shear flow. However, the model systems behave differently during relaxation. 13.5 wt % PBG in cresol exhibits an increase in orientation upon flow cessation, while the HPC solutions exhibit decreasing orientation during relaxation. These opposite trends were also seen in previous birefringence studies, where they were related to differences in the evolution of macroscopic rheological properties of the LCP solution during relaxation.

Finally, we have carried out preliminary experiments on a highly concentrated (40 wt %) solution of PBG in cresol. It has recently been reported that the rheological behavior of PBG solutions changes abruptly above concentrations of 35 wt %. Our x-ray scattering measurements suggest the presence of a more highly ordered phase in the 40% solution, that we have tentatively identified as hexagonal. At high shear rates, it appears that this ordered phase is disrupted, and a typical nematic scattering patterns such as is seen in Figure 1 is recovered. These phenomena will be the object of further detailed studies.

Figure 1. 2-D scattering pattern observed in 60 wt % HPC in water, subjected to shear flow at 100 1/s.

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Structural Measurements of $\text{NiS}_{2-x}\text{Se}_x$ *
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X18A

S. N. Ehrlich, G. L. Liedl, P. Metcalf, S. Soma and J. Honig (Purdue University)

Single crystals of $\text{NiS}_{2-x}\text{Se}_x$ were grown with compositions of $x = 0.51$, $x = 0.55$ and $x = 0.63$. For $x = 0.51$ and $x = 0.55$ a broad electrical and corresponding magnetic anomaly was encountered above $T = 40\text{K}$; the sample with $x = 0.63$ remained a poor metal. Powder diffraction measurements we have made for samples with $x = 0.51$ and $x = 0.55$ show no corresponding structural changes, such as a phase transformation, in the temperature range $T = 20\text{K} - 300\text{K}$. We have made room temperature measurements on single crystals of a sample with $x = 0.50$ which show multiple peaks in θ - 2θ scans of several different reflections, indicating regions of different lattice parameters within the sample. We measured these reflections just above and just below the Se K edge ($E = 12658\text{ eV}$) to search for an energy dependence in these multiple peaks. Preliminary results possibly indicate regions of varying Se concentration within the sample.

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XSCAN X-ray Data Acquisition and Analysis Software for the MATRIX X-18A X-ray Scattering Beam Line at the NSLS *

X18A

S. N. Ehrlich, J. A. Schwanof (Purdue Univ.), X. Yang (Howard Hughes Med. Inst.) and G. L. Liedl (Purdue Univ.)

A versatile and easy-to-use computer software package has been developed for equipment control, data acquisition and analysis at the MATRIX X-18A x-ray scattering beam line at the National Synchrotron Light Source. The software runs on any IBM compatible personal computer running under MS-DOS and makes use of the GPIB and AT-Bus interfaces. The menu driven program is user-friendly for a wide range of x-ray experiments through control of all aspects of the x-ray beam line. Equipment interfaces include counter-timer, stepping motor controllers, multi-channel analyzer and temperature controller. XSCAN can perform motions and scans in real space and reciprocal space and can do user designed scans using an external file scan capability, which reads in an ASCII file of positions for up to six diffractometer motions plus the x-ray energy and scans them in order. Integrated routines calculate orientation matrices for up to 20 reflections and can fit x-ray peaks using six different function types. Extensive help files are available and the data input is rigorously checked for proper form and consistency with software limits.

The XSCAN software has been evaluated by many users, both novice and experienced. Modifications have been integrated into the system to assist users. Plans are presently underway to upgrade the software to run under Windows NT complete with OLE support, multi-threading and Postscript capabilities.

* This work is supported by U.S. Department of Energy Grant No. DE-FG02-85ER45183.

The asymmetric shape of a multiple-diffraction peak yields information about the phases (ϕ) of the Bragg reflections involved[†]. The effect is particularly pronounced when, as a weak (P) reflection is rotated about its scattering vector, strong (H) reflections are simultaneously excited. Analyzing the resulting peak shape using n-beam perturbation theory[‡] gives a value for the triplet invariant, $\delta = \phi_P - H + \phi_H - \phi_P$. For a centrosymmetric structure, the only permissible values of δ are 0° or 180° .

Several multiple diffraction experiments have been performed on decagonal quasicrystals. These materials consist of periodically stacked planes. Precession photographs taken along the stacking axis reveal a quasicrystalline 10-fold rotational symmetry axis, indicating aperiodic order of the atomic sites within each plane. The purpose of this work is to investigate both the presence or absence of a center of symmetry, and the effect of stoichiometry on lattice locations.

The stoichiometries $Al_{68}Cu_{11}Co_{21}$ and $Al_{71}Ni_{24}Fe_5$ were studied. Since these different compositions produce diffraction patterns that have identical spot positions but different intensities, differences in the multiple-diffraction peaks reflect differences in atomic site locations. The figures below show intensity vs. ψ , the azimuthal angle of rotation about the weak reflection. For the $Al_{68}Cu_{11}Co_{21}$ system, all values of δ fell in the range 80° to 100° . For the $Al_{71}Ni_{24}Fe_5$ system, most values of δ indicated a centrosymmetric structure, with the exception of the reflection shown below. The positions of most multiple-diffraction peaks are reproducible in both alloys; different intensities and values of δ are observed. The analysis of these results is still in progress.

Figure 1.

We have investigated the effects of composition gradient on strain relaxation in compositionally graded $In_{1-x}Ga_xAs$ ($0 < x \leq 0.5$) buffers grown on GaAs substrates. The 5-step buffers were graded from In mole fraction $x=0$ to 0.5 , in increments $\Delta x=0.1$. Triple-axis x-ray diffraction measurements reveal nearly complete and isotropic strain relaxation in buffers with shallow and steep composition gradients. However, large differences in epilayer tilt and mosaic spread are observed. Fig. 1(a) and (b) present (004) maps of the buffers with 100 and 50 atomic % $In/\mu m$, respectively. These maps consist of a series of ω - 2θ scans with the same initial value of 2θ but a slightly different value of ω . In the plots, the y-axis corresponds to θ and the x-axis to ω ; the center value of ω in each ω - 2θ scan. Thus, the y-axis is a measure of d-spacing variations, and the x-axis is a measure of mosaic spread. The contours are lines of equal intensity, varying from 1,000 to 5,000 counts/second, in increments of 1,000. The GaAs substrate peak lies at $\theta=35.75^\circ$, and the 5 buffer steps lie at successively smaller θ . For the shallow-gradient buffer, fig. 1(b), the ω values of the epilayers and substrate peaks are essentially identical, indicating that the InGaAs planes are parallel to the GaAs planes. For the steep-gradient buffer, fig. 1(a), the ω values of the epilayers and substrate differ by as much as 1° , indicating that the InGaAs planes have tilted up to 1° with respect to the GaAs planes. More detailed contour maps in the vicinity of the top layers reveal differences in the broadening of ω scans, indicating greater mosaic spread in the steep-gradient buffer.

Figure 1. Triple-axis (004) contour maps, ω vs. θ , for buffers with gradients (a) 100 and (b) 50 atomic % $In/\mu m$.

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Ar-Sputtered Pt/Co Multilayers with Large Anisotropy Energy and Coercivity	X18A
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R. Harlow and P. Carcia (DuPont)

Pt/Co multilayers are candidates for a high density magneto-optical recording media. When Pt/Co multilayers are sputtered in Ar, however, they generally have smaller anisotropy energies and smaller coercivities than vapor-deposited multilayers. Since Ar-sputtering is preferred in manufacturing, we have sought methodologies that would simultaneously improve both the anisotropy (K_{eff}) and coercivity (H_c) of Ar-sputtered films. It has been found that the magnetic properties can be dramatically improved if the Pt/Co multilayers were sputtered on granular Pt underlayers made by etching thin Pt layers initially 20-40 Å thick. Multilayers grown on these Pt underlayers maintain a physically segregated, columnar microstructure with excellent (111)-fcc texture as determined by electron probe microscopies and in-house x-ray diffraction techniques. The desired magnetic properties reach a maximum when the Pt underlayer is approximately 33 Å and decrease substantial when the underlayer is either ca. 17 Å thicker or thinner. In-house x-ray diffraction measurements indicated that there was a strong correlation between the magnetic properties and the texture of the multilayer.

To examine the textural properties in more detail, three samples with Pt underlayer thicknesses of 17, 33 and 50 Å were studied at X18a using a very small focused beam (ca. 1 x 1 mm) and high-resolution optics (111-Ge analyzing crystal). Concentrating on the main peak from the 10x(3 Å Co + 8 Å Pt) multilayer, it was easily demonstrated that the rocking curve for the sample with the 33 Å underlayer was very sharp, 0.006 deg., while those of other two samples were quite broad, greater than 1.0 deg. The low-angle region of the 33 Å sample was in general characterized by a multitude of peaks and fine-structures corresponding to interferences between the different layers and surfaces. As expected, the other samples showed far fewer peaks in this region. Curiously, the main (111)-fcc reflection for all three samples was barely visible in the wide-angle diffraction scans. While the intensity of this peak was expected to be small for the 17 Å underlayer sample, this peak should have been nicely visible in the 33 Å sample because of its high texturing and in the 50 Å sample simply because of its thick Pt layer. Fixing the Bragg angle and scanning in both omega and chi failed to improve the situation. Thus, while these experiments have confirmed the earlier findings that the texturing of the 33 Å sample is higher than that in either the 17 or 50 Å cases, they have raised other questions about the nature of these films which are still unanswered.

Structural Studies of Self-Assembled Alkynyl Thin Film Materials	X18A
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A. K. Kakkar, C. M. Yam (McGill Univ.), A. Richter and P. Dutta (Northwestern Univ.)

Molecular self-assembly of functionalized chromophores at interfaces continues to draw significant attention due to potential technological applications of the resulting robust and highly ordered thin films in photonics, conductivity, catalysis etc. We have recently developed [1-2] a new chemical methodology for the molecular self-organization of i) long chain alkanes containing terminal alcohol, thiol and carboxylic acid groups; and ii) rigid-rod alkynes. An evaluation of the spatial relationships between constituent molecular building blocks which provide structural control at the molecular level, is an essential component of our research. We have undertaken a detailed structural study of the above mentioned interfaces by using ellipsometry and X-ray reflectivity. Monolayers of long chain alkanes with varying lengths and end groups, and rigid-rod alkynes with variable acetylenic microstructures were prepared on single crystal Si wafers using our new synthetic approach based on simple acid-base hydrolytic chemistry.

The X-ray reflectivity studies were carried out on X18A (Aug. 3-13, 1995) and X23B (Oct. 6-Nov. 5, 1995). These studies of the thin films containing alkynyl chromophores self-assembled by pure pi-pi interactions, constitute first examples of such an investigation. For long chain alkanes, the thicknesses and tilt angles are in good agreement with the ellipsometric data and earlier studies of such interfaces prepared using traditional synthetic routes [3]. A preliminary investigation of the X-ray reflectivity data on alkynyl thin films suggests a trend in the tilt angle related to the length of the rigid-rod and the electron density. A detailed structural investigation of these alkynyl thin films is currently being pursued.

1. C.M. Yam and A.K. Kakkar, J. Chem. Soc., Chem. Commun., 1995, 907-909.
2. M.G.L. Petrucci and A.K. Kakkar, J. Chem. Soc., Chem. Commun., 1995, 1577-1578.
3. A. Ulman, An Introduction to Ultrathin Organic Films, Academic Press, New York, 1991.

Interface Structure in ZnSe-GaAs Heterostructures *

X18A

V. Mahadev, S. N. Ehrlich, and G. L. Liedl (Purdue Univ.)

Three ZnSe-GaAs heterostructures, with different surface stoichiometries of (001) GaAs, were studied. They were MBE grown ZnSe on (i) As rich c-(4x4) GaAs, (ii) intermediate coverage (4x6) GaAs, and, (iii) As deficient (4x3) GaAs. Two thicknesses of ZnSe were examined, 15 and 100 nm. High resolution transmission electron microscopy studies indicated a formation of an interface compound in cases (ii) and (iii) but not (i). Grazing incidence x-ray Bragg-reflection-diffraction was utilized to analyze the interface structures in these heterostructure samples. Variable penetration relative to the interface depth was achieved relative to the thinner ZnSe by variation of the glancing angle from 0.12 to 0.5 degrees.

Out-of-plane scattering was measured for all samples with a systematic study of the fundamental reflections and all possible superstructure reflections. No superstructure reflections were observed in any of the three cases with either thickness of ZnSe. For the 15 nm ZnSe layer only the fundamental reflections were observed for ZnSe at 0.12 degree glancing angle that corresponds to an effective penetration of less than 15 nm. At the 0.36 degree glancing angle, just penetrating through the 15 nm ZnSe, broad peaks were observed on the high angle side of the fundamental reflections for cases (ii) and (iii) as shown in the figure below. At the 0.5 degree glancing angle only the fundamental reflections were again observed. These observations would indicate that the superstructure present at the time of deposition is not preserved in any of the three cases. In the As-rich case (i), the results would be consistent with an abrupt transition from the substrate to the thin film with no interface transition. In the Ga-rich cases the broad peaks observed are consistent with a thin strained transition layer. A simulation model based upon a tetragonally distorted, disordered Ga_2Se_3 interfacial layer fits the observed diffraction data.

Figure 1.

* This work is supported by U.S. Department of Energy Grant No. DE-FG02-85ER45183.

X-ray thermal diffuse scattering (TDS) study of the impurity effect on the anharmonic lattice dynamics for the para-to-ferroelectric phase transformation in $BaTiO_3$ *

X18A

N. Takesue, H. Kubo and H. Chen (Univ. of Illinois at Urbana-Champaign)

Addition of impurities may vary the Curie temperature (T_c) associated with the para-to-ferroelectric phase transition in terms of the lattice harmonicity and anharmonicity. One of the purposes of our research is to make clear the role of impurities through the anharmonic dynamics in a prototypical perovskite ferroelectric $BaTiO_3$.

Two $BaTiO_3$ single crystals with one containing 0.3 at% Fe^{3+} substitutionally replacing for Ti^{4+} have been examined by *in-situ* x-ray thermal diffuse scattering (TDS) measurement near T_c at X18A. Results from the pure sample show two-dimensional TDS distribution around the Bragg peaks on the 100 relplane; they are attributed to the overdamped [010] TO mode and to the anisotropic on-(100) TA modes [1]. The TDS distribution and temperature dependence of the intensity (Fig. 1) agree well with the previous neutron inelastic scattering results.

The TDS distribution from the Fe-doped sample shows a similar pattern to that of the pure sample. However, it also displays a different (positive) temperature dependence of the intensity (Fig. 2) as well as a more isotropic distribution for small q 's. Impurities may have reduced the anharmonic interatomic force constants. Currently, the TDS calculation is being done through the normal mode analysis based upon the rigid shell model for both samples.

[1] N. Takesue, M. Maglione and H. Chen, Phys. Rev. B51, (1995) 6696.

Figure 1. TDS vs. q [010] for the pure sample (left), and for the doped sample (right).

* This work is supported by the U.S. Department of Energy

In situ X-ray Diffraction Studies of YBCO/LaAlO ₃ Superlattices	X18A
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S. Williams and J. B. Ketterson (Northwestern Univ.)

We have constructed a multi-target sputtering cell equipped with mylar windows, enabling us to study the growth of multi-layer films in situ. The faced magnetron sputtering guns have four targets, with the active target selected by rotating the cathode. In this way, multi-layer films can be deposited while the substrate remains fixed, preserving the x-ray alignment.

Our most recent studies have involved the growth of YBa₂Cu₃O_{7-x}/LaAlO₃ superlattices. A good lattice match and perovskite structure make LaAlO₃ ideally suited for YBCO. We were able to grow high quality superlattices with satellite peaks of up to fourth order. Since our sample cell allows us to study the films in real time, we were able to observe the effects on annealing on the quality of the films by observing the decay of the satellite peaks. We used a program written by Eric Fullerton in order to fit the superlattice spectra and determine the degree of interdiffusion and roughness in our layers. We found no change in the superlattice spectra when the annealing temperature was below 800°C. Above this temperature, we observed a decay in the satellite peaks corresponding to increased interdiffusion at the interfaces.

Epitaxial Growth of n-Alkane Monolayers on a Ag(111) Surface *	X18A
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Z. Wu, J. Wang, (Univ. of Missouri-Columbia) S. N. Ehrlich, (Purdue Univ.) B. Matthes, K. W. Herwig and H. Taub (Univ. of Missouri-Columbia)

Synchrotron x-ray diffraction has been used to study the structure of butane (n-C₄H₁₀), hexane (n-C₆H₁₄), and heptane (n-C₇H₁₆) monolayers adsorbed on a single-crystal Ag(111) surface, complementing previous neutron diffraction experiments with deuterated forms of these monolayers on an exfoliated graphite substrate¹⁻³. The unit cell of all of these monolayers on graphite is rectangular with a herringbone arrangement of the molecules for butane² and hexane¹ and a rectangular-centered cell for heptane³. We have found that on the Ag(111) surface, the monolayers grow with a well-defined orientational relationship with the substrate apparently forming a higher-order commensurate structure. The structural parameters, including the monolayer orientation, are given below. It has been assumed that the butane and hexane unit cells remain rectangular as on graphite. For a monolayer of (n-C₄H₁₀) the lattice constants are $a = 8.11\text{\AA}$ and $b = 7.49\text{\AA}$ and the monolayer orientation is G₂₀ 18 deg from Ag(10) azimuth. For a monolayer of (n-C₆H₁₄) the lattice constants are $a = 16.1\text{\AA}$ and $b = 5.20\text{\AA}$ and the monolayer orientation is G₂₁ 14 deg from Ag(10) azimuth. For a monolayer of (n-C₇H₁₆) the lattice constant is $d_{11} = 4.69\text{\AA}$ and the monolayer orientation is G₁₁ 12.5 deg from Ag(10) azimuth.

For the hexane/Ag(111) system, specular reflectivity measurements are consistent with the adsorbed molecules oriented with their carbon skeletal plane parallel to the Ag(111) surface as on graphite. Also, the monolayer lattice parameters give the same area of the unit cell as on graphite. We observe a 0.5% thermal expansion of the monolayer between 120 K and the melting point at 151 K. Coincident with this expansion, the monolayer rotates 0.12 deg further away from the Ag(10) azimuth.

It would be interesting to see whether the orientational epitaxy and rotation of these n-alkane monolayers on the Ag(111) surface can be understood in terms of theories previously applied to simpler molecules on graphite^{4,5}.

1. H. Taub, in *The Time Domain in Surface and Structural Dynamics*, NATO ASI, Vol. 228, Ser. C (Kluwer, Dordrecht, 1988), p. 467.

2. K. W. Herwig, J. C. Newton, and H. Taub, *Phys. Rev. B*, **50**, 15287 (1994).

3. B. Matthes, K. W. Herwig, and H. Taub, unpublished.

4. A. S. Novaco and J. P. McTague, *Phys. Rev. Lett.*, **38**, 1286 (1977).

5. F. Grey and J. Bohr, *Europhys. Lett.*, **18**, 717 (1992).

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Y. Zhang, R. Colella, S. N. Ehrlich (Purdue Univ.), S. Kycia and A. Goldman (Iowa State Univ.)

It is of interest to study the distribution of diffuse scattering surrounding Bragg reflections in a nonperiodic crystal, because useful information may be obtained for a better understanding of the atomic structure. A photograph (Fig. 1) was taken using a monochromatic x-ray beam ($\lambda = 0.711 \text{ \AA}$) impinging on a stationary thin slice of Al-Pd-Mn quasicrystal, about 0.38 mm thick, set perpendicular to the beam. A two-fold axis direction was parallel to the x-ray beam. The photographic film was placed behind the crystal, perpendicular to the x-ray beam. Our attention concentrated on the four spots marked by arrows, which are "clouds" of diffuse scattering surrounding Bragg spots located on two-fold axes. The distribution of diffuse scattering surrounding those four Bragg reflections is very irregular. However, the crystal region responsible for the diffuse scattering visible in the photograph is very perfect. A rocking curve taken with the same x-ray beam, in a symmetric Laue-case geometry, yielded a rocking curve whose width was resolution limited (≈ 30 arcsecs.). Detailed (hkl) scans, taken along planes perpendicular to a two-fold axis direction, revealed a very complicated structure of diffuse scattering, with no resemblance to the expected $1/q^2$ dependence. Figure 2 is an example. The Bragg reflection is located at the center, "behind" the plane of the figure. Plans are under way to explore the diffuse scattering surrounding other Bragg reflections, and to see the effect of temperature.

Figure 1.

Figure 2.

R.J. Davis, Z. Liu, J.E. Tabora, and W.S. Wieland (U. Virginia)

The first structural characterization by Ti K edge EXAFS and XANES of ETS-10 and aluminum-free Ti-beta molecular sieves was performed [Davis et al. Catal. Lett. 34, 101 (1995)].

A TS-1 sample was also studied for comparison. The near edge spectrum of TS-1, shown in Figure 1, revealed an intense pre-edge feature characteristic of Ti atoms in tetrahedral coordination. However, the pre-edge peak for ETS-10 in Figure 1 was quite small and shifted in energy, which is consistent with the known octahedral structure surrounding Ti atoms in the material. Analysis of the EXAFS for ETS-10 revealed an average Ti-O interatomic distance of 2.00 ± 0.01 which is longer than the Ti-O distance (1.95) in anatase. For Ti-beta, an intense pre-edge peak is present in the near edge spectrum and the intensity, energy and width of this peak are the same as for TS-1.

In addition, the average Ti-O interatomic distance in Ti-beta and TS-1 was 1.80 ± 0.01 , which is significantly shorter than the distance measured in ETS-10. The EXAFS and XANES results indicate that the Ti sites in aluminum-free Ti-beta are structurally identical to the tetrahedral sites in TS-1. This conclusion is supported by the similarity of the UV absorption thresholds for the two samples.

X-ray absorption spectra were also recorded with methanol or 2-propanol adsorbed on the Ti-beta and TS-1 molecular sieves. Alcohol adsorption decreased the intensity and broadened the Ti pre-edge peak for both samples, demonstrating a local chemical interaction with the Ti sites. Methanol adsorption lengthened the average Ti-O bond to 1.83 ± 0.01 . The similarity of the x-ray absorption spectra for aluminum-free Ti-beta and TS-1 in the presence of alcohols suggests that the Ti sites in the two frameworks are chemically indistinguishable for vapor-phase adsorption of alcohols at low concentrations.

Figure 1. Ti K edge spectra for ETS-10, TS-1 and Ti-beta zeolites.

* This work was supported by the National Science Foundation (CTS-9257306) and the donors of the Petroleum Research Fund administered by the ACS (24446-G5).

Renovation of Beamline X-18B for High Energy X-ray Spectroscopy X18B

S. Khalid, L. Furenlid and P. Siddons (BNL)

The beamline X-18B is back in operation since August 1995 under the NSLS management and support. The old Galvachenko type monochromator and its housing has been replaced with a new Si(111) channel cut monochromator inside a cross chamber for an easy access for repairs and modifications.

The new monochromator is under 10^{-8} - 10^{-9} torr vacuum and it is water cooled with the gravitational flow and water pump circulation system. This avoids any mechanical vibrations and temperature variations. The first crystal has a water cooled copper backing block with an indium-gallium liquid eutectic alloy in between for improved surface contact and thermal conduction. The harmonic rejection is achieved by rotating the second crystal at its weak link using a spring loaded micrometer. The energy is scanned by rotating the first crystal along its central axis by a 30 cm lever arm outside the housing, linearly driven by a micrometer and a five phase motor system.

The energy range of this monochromator is 8 - 31 KeV with an energy resolution of about 10^{-4} . The 3 eV wide kink, typical of a copper metal edge is highly resolved when a 0.3 mm slit is being used at the upstream of the monochromator (fig. 1).

The ion chamber current output of this spectrometer was also measured and it was found comparable to other beamlines and to the expected theoretical values (fig. 2).

The separation between the crystals is only 3.5 mm and therefore the variation in the exit height of the beam is negligible. In the worst case of Ni - EXAFS (K-edge at 8.333 KeV) it is less than 45 microns for a typical 1200 eV scan. One disadvantage of the channel cut is the presence of multiple beams at the outlet, however, once the fundamental beam is identified a laser inside the hutch is used as a reference to keep track of that beam. In addition the crystals can also rotate in chi direction which sometimes can be used to displace the position of crystal glitches if they appear at a sensitive position in an XAS spectrum.

Figure 1. Energy resolution at copper edge.

Figure 2. Current output from Si(111) X18B channel cut mono. Beam current normalized to 100 mA, N_2 flow in 10 cm ion chamber. 20 m from the source (fully tuned).

Chlorine XANES Analysis of Stepwise Combustion Tests on Coal * X19A

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The release of chlorine from high chlorine (>0.3 wt) investigated by means of Cl K-edge XANES of stepwise combustion tests. The coals were exposed to air at 50°C temperature intervals between 200°C and 800°C for an hour and the residues (char or ash) were subsequently examined by Cl XANES spectroscopy at room temperature using a standard Lytle fluorescence X-ray detector. Although the XANES spectra of Cl in both untreated coals are closely similar, the results indicate different Cl-containing intermediate compounds are formed for the two coals. The English coal, but not the Illinois coal, exhibits the formation of NaCl in the vicinity of $200 - 300^\circ\text{C}$ (note small peak at 12 eV in Figure 1) and both coals appear to exhibit organo-chlorine species (note sharp peak at -1 eV in Figure 1) in the chars formed at somewhat higher temperatures ($300 - 500^\circ\text{C}$). Based on the reduction of the step-height of the Cl K-edge, the concentration of chlorine remaining in the char or ash formed at temperatures above 400°C is less than 10% of that of the original coal (Figure 2).

These data are being used (i) to explain the variable behavior of chlorine in combustion of different coals; (ii) to understand the corrosiveness of Cl in combustion of high-Cl coals; and (iii) to establish whether significant volatile organochlorine forms can be formed during coal combustion.

Figure 1. Left: Cl XANES of coal as a function of temperature. Right: Variation of the chlorine content as a function of temperature.

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STRUCTURAL CHARACTERIZATION OF PHENYLCOPPER IN THF SOLUTION

X19A

H. Huang and J.E. Penner-Hahn (The University of Michigan)

In previous work, we have characterized the structure of organocuprate and cyanocuprate reagents in THF solution [1-4]. These studies demonstrated that the dominant Cu species in solutions formed from $\text{CuX} + n\text{RLi}$ ($\text{X} = \text{CN}$, $\text{R} = \text{Me}$, Bu , Ph , $n = 1, 2$; and $\text{X} = \text{I}$, $\text{R} = \text{Me}, \text{Ph}$, $n = 2$) were mononuclear alkylcyano-, dialkyl-, or diarylcuprates. The only example of oligomerization that we found was in the case of the parent material, $\text{CuCN} \cdot 2\text{LiCl}$, which appears to form $(\text{Cu}-\text{CN}-\text{Cu})_n$ oligomers [3]. In the present report, we describe the recent extension of these studies to include the characterization of phenyl copper reagents. In these systems, we find clear evidence for oligomerization.

Phenyl copper (and related reagents) have proven to be extremely versatile in organic synthesis. For example, it was reported that phenyl copper can be used to stereospecifically deliver a phenyl group to conjugated enones. The Fourier transform of the EXAFS data for 0.2 M phenylcopper, prepared by the addition of one equivalent of phenyl lithium to Copper(I) iodide, is shown in the Figure. It is clear that there are substantial outer shell peaks in these data. The peaks at $R + \alpha \approx 1.5$, 3.3, and 4 Å are consistent with those expected for a Cu-phenyl interaction. Curve fitting results using FEFF 5.0 suggest that these are most consistent with the presence of a single phenyl group bound per Cu. The remaining peak, at $R + \alpha \approx 2$ Å is significantly more intense than any of the Cu-C peaks. The large peak can only be modelled by including a Cu-Cu scatterer at ca. 2.45 Å. This distance is 0.1 Å shorter than the Cu-Cu distance in Cu metal, suggesting that this feature is not due to contamination of the solutions by Cu decomposition products. This short Cu distance is consistent with the Cu-Cu distances seen in previously crystallized pentameric phenyl-copper clusters, suggesting that similar species are present in THF solutions of phenyl-Cu.

[1] Barnhart, T. M.; Penner-Hahn, J. E. *Physica B* 1995, 208-209, 709-710. [2] Barnhart, T. M.; Huang, H.; Penner-Hahn, J. E. *J. Org. Chem.* 1995, 60, 4310-11. [3] Stemmler, T. L.; Barnhart, T. M.; Penner-Hahn, J. E.; Tucker, C. E.; Knochel, P.; Bohme, M.; Frenking, G. *J. Am. Chem. Soc.* 1995, in press. [4] T. Stemmler; Penner-Hahn, J. E.; Knochel, P. *J. Am. Chem. Soc.* 1993, 115, 348-350.

Figure 1.

Magnetic properties of Ni Porphyrins

X19A

M.W. Renner (DAS), K.M. Barkigia (DAS), J. Fajer (DAS), L.R. Furenlid (NSLS)

Metalloporphyrin p-cation radicals are models for the active sites in a variety of biological systems including photosynthesis and heme catalysis. How the unpaired electrons of the metal and oxidized porphyrin interact is important to understanding the reaction chemistry in these biological processes.

The relative symmetries of the macrocycle and metal d-orbitals which contain the unpaired electrons have been proposed to be responsible for the two spins interacting via ferromagnetic or antiferromagnetic coupling.

We have recently been investigating a series of sterically crowded metalloporphyrins in which the macrocycle adopts a distorted S4 saddle conformation.

The low-spin Ni(II) complex is unable to bind axial ligand to form a high-spin species. One electron oxidation of the Ni(II)P (P = octaethyltetraphenylporphyrin) affords a macrocycle centered radical. Upon addition of bases (methanol, pyridine, etc.) results in an EPR spectra characteristic of a Ni(III) porphyrin. However, from x-ray crystallography the Ni-N distances (about 2.0 Å) are characteristic of a high-spin.

To resolve the issue of the nickel's oxidation state and magnetic properties we have studied the Ni x-ray absorption near-edge structure (XANES).

The metal's edge energy has been shown to be sensitive to the oxidation state of the metal. The XANES spectra for Ni(II)P and one-electron oxidation product of Ni(II)P + pyridine are shown in the figure below. The edge position remains constant for both samples, therefore the macrocycle is oxidized. The loss of the pre-edge peak indicates that the pyridine coordinates to the Ni(II) in the oxidized sample. To explain the EPR and crystallographic data the nickel must be high spin ($S = 1$) and antiferromagnetically couple with the macrocycle radical ($S = 1/2$) to afford a pseudo ($S = 1/2$) Ni(III). The saddle shaped distortion in the macrocycle appears to be essential for magnetic interaction between the unpaired electrons of the macrocycle and metal d orbitals.

Structural Studies of Ni(II) Porphyrins *

X19A

Mark W. Renner, Kathy M. Barkigia, Jack Fajer (BNL - Dept. of Applied Science), Lars R. Furenlid (NSLS),

Metalloporphyrins are the prosthetic group in a variety of biological systems. The structure of these porphyrins is believed to be important in altering their reactivity and physical properties. The metal-nitrogen distances in porphyrins are sensitive to conformational changes in the macrocycle, shorter distances reflect increased distortions. We present here a comparison of the Ni-nitrogen distances for a series of Ni(II) porphyrins as determined by EXAFS and single crystal X-ray diffraction. The porphyrins studied have meso substituents which increase in size from methyl (1) < propyl (2) < isopropyl (3) < tert-butyl (4).

The Ni-N distances from solution EXAFS for 1 and 2 are on the average 0.06 shorter than the single-crystal X-ray and EXAFS distances. For this series the Ni-N distances decrease as the size of the meso groups increase. Steric interaction with the larger meso substituents and the macrocycle causes the porphyrin to distort. Comparison of the solution and single-crystal results for 1 and 2 confirm that these porphyrins have multiple conformations of similar energy in solution and in the solid state. Some care must be used when extrapolating single crystal x-ray diffraction results to the macrocycles conformation in solution or in the biological systems.

Compound	R (Å) EXAFS	R (Å) X-ray
1	1.91	1.953
2	1.90	1.957
	1.96*	
3	1.91	1.896
4	1.84	--

* single crystal EXAFS.

Figure 1.

* This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, D.C., under contract No. DE-AC02-76CH00016.

Single Crystal EXAFS Studies of Nickel(II) Porphyrins

X19A

M.W. Renner, J. Fajer, and K.M. Barkigia (BNL - Dept. of Applied Science), and L.R. Furenlid (NSLS)

Metalloporphyrins are the prosthetic group in a variety of biological systems and the structure of these porphyrins are important in controlling their reactivity and physical properties.

The metal-nitrogen distances are generally sensitive to conformational changes in the macrocycle, shorter distances reflect increased distortions. We present here a comparison of the Ni-nitrogen distances for a Ni(II) porphyrin as determined by solution and single-crystal EXAFS and compare these results with single crystal X-ray diffraction.

The crystal was oriented using a goniometer and measurements were taken in fluorescence mode using a 13-element solid state detector. The structure of the Ni(II) porphyrin studied and the XANES as a function of the crystal orientation are shown below. When varying the orientation of the molecular xy plane, which contains the nickel and four nitrogens, from perpendicular to parallel relative to the incoming beam polarization direction, the pre-edge decreases in intensity. These results provide proof that this transition has z character; it has been proposed to be a 1s-4pz transition as in square planar copper compounds.

Analysis of the EXAFS data reveals that the porphyrin has different solution and solid state conformations. The Ni-N distances in solution (1.90 Å) are 0.06 Å shorter than the single-crystal X-ray (1.957 Å) and EXAFS (1.96 Å) distances. These differences might results from crystal packing forces or solvations effects.

We conclude that one must be cautious when extrapolating single crystal X-ray diffraction results to solution conformations.

Ni(II) tetra-propyl porphyrin

Naresh Shah, Jianmin Zhao, Fulong Lu, Frank E. Huggins and Gerald P. Huffman (University of Kentucky)

We have designed and constructed an in-situ cell for XAFS investigation of direct coal liquefaction (DCL) catalysts (figure 1). This design of cell can reproduce elevated temperature (up to 500 °C) and hydrogen pressure (up to 1800 psig hydrostatic pressure) employed in the liquefaction reactors while letting a synchrotron generated x-ray beam pass through.

Using this cell, several catalyst systems have been successfully examined: (1) Black thunder coal ion-exchanged using iron acetate solution to get 3.78 wt.% Fe loading, (2) 5 wt.% of binary ferrihydrite catalyst (containing 5 wt.% SiO₂) in Blind Canyon (DECS-17) coal and (3) 5 wt.% of citric acid treated ferrihydrite catalyst in Blind Canyon (DECS-17) coal. All three iron-based catalyst systems investigated, exhibited transformation of the iron oxyhydroxide phase to pyrrhotite. The transformation temperatures were different for different systems. This transformation occurred over a range of temperature conditions. This lack of a sharp transition can be due to either (1) a nonhomogeneous transition within the sample matrix, i.e., some (smaller?) catalyst particles transform at a lower temperature and some at a little higher temperature, or, (2) there are more than one transformation. The results clearly demonstrated that the kinetics of the ferrihydrite to pyrrhotite transformation are dependent on the dispersion and the structure of the ferrihydrite.

Figure 1. Schematic of the high pressure high temperature XAFS cell for in situ characterization of direct coal liquefaction (DCL) catalysts.

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D.L. Tierney, R.J. Denver, and James E. Penner-Hahn (Univ of Michigan)

In recent years, Zn has come to be recognized as an essential trace element in a tremendous range of biological functions [1], and has been suggested [2] to be a major regulatory ion in metabolism. For example, the pool of labile Zn (i.e., accessible to chelators), increases synchronously with the onset of apoptosis (active cell death) [3]. At the other end of the developmental spectrum, decreases in free Zn are teratogenic [4]. Despite the obvious importance of Zn, relatively little is known about the mechanisms by which it regulates cell growth and development.

Eggs that develop in closed conditions (i.e., without the influx of maternal nutrients during development) must contain, at the time of fertilization, all of the metals that are necessary for development. Typical levels are ca. 1 mM Zn and 0.5 mM Fe, with lower levels of other essential trace elements [5]. We have recently shown that the average structure of the Zn in zebrafish eggs, as determined by XANES, changes during the early stages of development [6]. Following fertilization, but prior to the mid-blastula transition (MBT), there is an increase in the white line intensity. After the MBT, the average Zn environment is similar, but not identical, to that found in the unfertilized eggs. Recently, we have extended this work in an effort to determine if these spectral changes are similar across species. We used *Xenopus* (African clawed frog) eggs, since these have volumes that are nearly an order of magnitude larger than those of zebrafish eggs, thus permitting measurements on single eggs. The Figure shows difference XANES spectra for fertilized eggs after the MBT minus unfertilized eggs. It is clear that similar difference spectra are seen for fish and frogs. We are presently extending these results to characterize the detailed time dependence of the Zn structure.

[1] Vallee, B.; Falchuk, K. *Physiol. Rev* 1993, 73, 79-118. [2] Frausto da Silva, J.; Williams, R. In *The Biological Chemistry of the Elements* Clarendon Press: Oxford, 1991; pp 299-318. [3] Zalewski, P.; Forbes, I.; Seamark, R.; Borlinghaus, R.; Betts, W.; Lincoln, S.; Ward, A. *Chemistry Biology* 1994, 1, 153-161. [4] Hornvall, H.; Falchuk, K.; Geraci, G.; Vallee, B. *Biochem. Biophys. Res. Commun.* 1994, 200, 1398-1406. [5] Nomizu, T.; Falchuk, K.; Vallee, B. *Mol. Reprod. Dev* 1993, 36, 419-23. [6] Walrath, L.; Tierney, D.; Penner-Hahn, J.; Berg, J. 1996, in preparation.

Figure 1. Difference XANES for eggs after MBT minus unfertilized.

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Sulfonate Sulfur and not the Sulfide Sulfur Dominates the Composition of Marine Phytoplankton *

X19A

Murthy A. Vairavamurthy, S. Wang, B. Khandelwal and B. Manowitz

Living organisms play an important catalytic role in the environmental and geochemical transformations of sulfur, changing the chemical properties of sulfur compounds and their distribution in the atmosphere, soils, waters and sediments. In the oceans, sulfur transformations are largely mediated by phytoplankton which assimilate seawater sulfate as the sole sulfur source to make the reduced organic sulfur compounds. The biosynthesized organic sulfur in marine phytoplankton comprises 0.5 to 1 basis, and includes a variety of functional forms. Major forms of this sulfur include organic sulfides, sulfonium compounds, sulfonates, and sulfate esters. The relative quantitative composition of the various forms are not known. Several studies suggest that sulfonium compounds, particularly dimethylsulfonium propionate (DMSP), constitute an important fraction of cellular organic sulfur in some phytoplankton species, but it is generally believed that sulfide sulfur is the dominant form. Recently, sulfonates were found to be a major class of compounds in near-surface marine sediments, constituting about 20-40 and phytoplankton debris was invoked as a possible source for their origin, among other potential mechanisms. A variety of marine algae are known to contain sulfonates, but if they are to be a major source of sedimentary sulfonates, then they must contain high levels of these compounds. In an attempt to better understand the composition of the different forms of sulfur in phytoplankton, we used x-ray absorption near-edge structure (XANES) spectroscopy for both qualitative and quantitative speciation of sulfur. Figure 1 shows XANES spectra of some phytoplankton species representing major types in the oceans, diatoms, dinoflagellates, prymnesiophytes and chlorophytes. We deconvoluted these spectra with spectra of model compounds to obtain quantitative information of the sulfur forms present. Our results show that the oxidized sulfonate sulfur and not the reduced sulfide sulfur as the dominant form of sulfur in phytoplankton. The presence of high concentrations of sulfonate-sulfur in phytoplankton suggests that the latter could be a major source of sedimentary sulfonates. Furthermore, the dominance of sulfonates suggests that they play an important role in the cellular biochemistry and physiology of marine phytoplankton, which are still unknown.

Figure 1. Sulfur K-edge XANES spectra of different types of phytoplankton

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Di- and Polysulfide Cross Linking in the Formation of Humic Polymers in Marine Sediments *

X19A

M.A. Vairavamurthy, W. Zhou and B. Manowitz (BNL)

Biogenic organic matter that was buried in sediments mostly under anaerobic conditions lead to the formation of fossil fuels after being subjected to a series of chemical transformations occurring over geological time. Important steps in these conversions include the initial formation of macromolecular sedimentary humic polymers from the biopolymers of aquatic plant and animal remains, and the subsequent but continuous transformation of the humic polymers to the petroleum-forming aquatic kerogen. It is believed that sulfur incorporation affects the preservation of organic matter, but the chemical mechanisms are not well understood. We used XANES spectroscopy to investigate whether di- and polysulfide linkages are involved in the formation of humic polymers in anaerobic marine sediments. The approach was to treat the humic acids with tributyl phosphine, a di- and polysulfide cleaving reagent, and to examine the changes in XANES spectra before and after treatment with tributyl phosphine. As Figure 1A shows for simple model compounds (benzyl disulfide and trisulfide), the shape of the XANES spectra change when treated with tributyl phosphine because of the formation of sulfhydryl groups. Figure 1B shows a similar effect for sedimentary humic acids isolated from a salt marsh in Shelter Island, suggesting that di- and polysulfide linkages are indeed involved in forming humic polymers in reducing marine sediments. We determined by liquid chromatography two major low-molecular-weight thiols, 3-mercaptopropionic acid and methane thiol, among the compounds released from tributyl phosphine treated humics. According to previous studies, these thiols can be easily degraded by sedimentary bacteria. However, both thiols were present as components of the humic substances throughout the sediment column, down to the 22 cm depth sampled, suggesting that incorporation into humic polymers, in fact, provides a mechanism for preventing mineralization of the bound organic matter. In general, humic polymers are resistant to microbial degradation because of their randomly polymerized structure. Thus, in reducing sediments, sulfur can play an important role in the preservation of sedimentary organic matter during early diagenesis by enhancing the formation of humic polymers through di- and polysulfide cross linking.

Figure 1.

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Investigation of Dislocation Distributions in InP single crystals Using Synchrotron White Beam X-ray Topography *

X19C

H. Chung, W. Si, M. Dudley, and V. Prasad (SUNY Stony Brook), A. Anselmo and D. F. Bliss (US Air Force Rome Laboratory)

Synchrotron White Beam X-ray Topography (SWBXT) has been applied to investigate dislocation distributions in a transverse cut InP wafer grown by the liquid encapsulated Kyropoulos (LEK) technique. Our preliminary results reveal that the dislocation density is higher near the periphery and the middle of the crystal and reaches a minimum in the intermediate area. Figure 1 is an enlargement of a transmission X-ray topograph recorded near the periphery of the crystal. As revealed by the image, a dislocation network with uniform density is evidenced. Since the dislocation density is at just about resolution limit, a dislocation density of approximately 10^5 cm^{-2} can be deduced from the topograph. In contrast to Figure 1(a), Figure 1(b) is a transmission X-ray topograph recorded from the intermediate region of the sample showing a very low dislocation density, in which individual dislocations (D) were clearly discerned. Since dislocation propagation and multiplication can occur when thermal stresses induced by thermal gradient during crystal growth and post-growth cooling processes are higher than the critical resolved shear stress (CRSS), our observations strongly suggest that a high level thermal stress is concentrated in the periphery and the middle of the crystal. Therefore, an optimization of thermal conditions is expected to be important to the reduction of dislocation density in these crystals.

Figure 1.

* Acknowledgments: Research carried out under auspices of the ARPA/AFOSR Consortium of Crystal Growth Research (Contract No. F496209510407), work performed on the Synchrotron Topography Project, Beamline X-19C.

Characterization of structure defects in 2,12-Undecanedione/Urea single crystals by Using Synchrotron White Beam X-ray Topography *

X19C

H. Chung and M. Dudley (SUNY Stony Brook), M. E. Brown and Mark D Hollingsworth (Indiana University)

In the urea inclusion compounds, the hexagonal host (urea) structure contains linear, parallel, non-intersecting channels (tunnels) with guest molecules closely packed along the channels. The periodic repeat distance (c_g) of guests is incommensurate with the periodic repeat distance (c_h) of the host along the channel-axis (i.e., c-axis). The structural properties and, especially, the packing arrangements of guest molecules in these incommensurate channel inclusion compounds are of interest. In the study presented, Synchrotron White Beam X-ray Topography (SWBXT) is applied to investigate structural properties and interchannel arrangements of guest molecules in 2,12-tridecanedione/urea inclusion compounds. Figure 1 shows a Laue diffraction pattern recorded from the sample. As revealed by the pattern, the crystal contains two sets of domains, each set showing 3-fold symmetry. The orientations of the two settings are related by 180° rotation about the c-axis. This observation reveals that the 6-fold symmetry of the host structure is reduced to two sets of 3-fold symmetry. Figure 2 (a) and (b) are enlarged X-ray topographs showing the detailed structures of these two settings. Our observations strongly suggest that the guest molecules can adopt rhombohedral packing arrangements, i.e. obverse and reverse settings. The structural requirements for the formation of this kind of twinning are still under investigation.

Figure 1.

* Acknowledgments: Work performed on the Synchrotron Topography Project, Beamline X-19C.

Figure 2.

Studies of Twinning in 2,10-Undecanedione/Urea Inclusion Compounds Using Synchrotron White Beam X-ray Topography *

X19C

H. Chung and M. Dudley (SUNY Stony Brook), M. E. Brown and Mark D. Hollingsworth (Indiana University)

Twinning in 2,10-undecanedione/urea was investigated by using Synchrotron White Beam X-ray Topography (SWBXT). X-ray transmission topographs recorded from different regions show that the crystal is divided into five twin-related regions. Each region in the crystal is revealed on the topographs by orientation contrast arising from the mutual misorientation of adjacent regions. Using a combination of pinhole Laue pattern analysis and topographic orientation contrast analysis, the twin operation was determined. The twin structure in this specimen can be represented using stereographic projections as shown in Figure 1. In this figure, the orientation relationships of these twin related regions are revealed; the contact points of these projections label the poles of the composition planes. The rotation angle, which would be exactly 60° if it were hexagonal, ranges from 59.1° to 61.8° , as determined by measuring the angles between the $[010]$ - $[130]$, $[130]$ - $[\bar{1}30]$ and $[130]$ - $[0\bar{1}0]$ directions from pinhole Laue diffraction patterns.

Figure 1.

* Acknowledgements: Work performed on the Synchrotron Topography Project, Beam-line X-19C.

Synchrotron White Beam X-ray Topography Characterization of Structural Defects in 2,10-Undecanedione/Urea Inclusion Compounds *

X19C

H. Chung and M. Dudley (SUNY Stony Brook), M. E. Brown and Mark D. Hollingsworth (Indiana University)

Twin structures in a crystal of the urea inclusion compound (UIC) of 2,10-undecanedione were investigated using Synchrotron White Beam X-ray Topography (SWBXT). Twin configurations, directly observed via orientation contrast, were found to comprise both large-volume, macroscopic twins and thick twin lamellae. Upon detailed analysis, one can find that there were five superimposed diffraction patterns in the crystal studied. This observation indicates that the crystal was divided into five twin-related regions (indicated by T_1 to T_5) with different relative orientations. Other defects such as inclusions and dislocations (indicated as I and D, respectively) were also observed. Detailed analysis of contrast variations of dislocations in different reflections shows that the dislocations are out of contrast when reflections with g vectors perpendicular to their line directions are used. By using the $g \cdot b = 0$ criterion, one can determine that these dislocations are of screw character with Burgers vector parallel to the $[130]$ direction.

Figure 1.

* Acknowledgements: Work performed on the Synchrotron Topography Project, Beam-line X-19C.

Characterization of Structural Defects in HgCdTe Epilayers by Using Synchrotron White Beam X-ray Topography *

X19C

H. Chung and M. Dudley (SUNY Stony Brook), Sanghamitra Sen (Hughes Santa Barbara Research Center)

An LPE grown HgCdTe (MCT) layer on a (111) CdZnTe (CZT) substrate has been studied by using Synchrotron White Beam X-ray Topography (SWBXT). The sample was step etched to leave regions with epi thicknesses ranging from 0 to 17 microns. Figure 1 (a) shows an X-ray topograph recorded in reflection geometry. A well-defined crosshatch pattern extended through the thickness of the layer to within 4.5 microns from the substrate. In the crosshatch-free region, a mosaic pattern was observed. From detailed investigations of the structure of cross hatching, one can find that the pattern comprises slip band networks lying along the three $\langle 110 \rangle$ directions. Figure 1 (b) shows an enlarged X-ray topograph in which individual dislocations are clearly visible. By calculating the projected length and directions of dislocation segments in different reflections, one can determine that these dislocations belong to the $[011]/(1\bar{1}1)$ slip system. Perhaps due to the influences of interdiffusion of substrate and layer components and the resulting mismatch between the substrate and the grown layer, the two regions with epi thickness of 0 and 3 microns, respectively were highly strained. It is also worth noting that defects such as a 180° rotation twin (T) and Te precipitates (P) and the associated prismatic punching of dislocation loops in star-like patterns are also revealed on Figure 1 (a). From the distribution of the cross-hatching which initiates from the periphery and propagates into the interior of the sample, one can expect that slip processes occur to relieve stresses concentrated at the periphery of the wafer induced either by thermal gradients or by the mechanical fasteners which support the wafer.

Figure 1.

* Acknowledgements: Work performed on the Synchrotron Topography Project, Beamline X-19C, and supported by Hughes Santa Barbara Research Center

Synchrotron White Beam X-ray Topography Studies of Interfacial Dislocations in SiGe/Si Heterostructures *

X19C

H. Chung and M. Dudley (SUNY Stony Brook), J. Wu (General Instrument)t

Synchrotron White Beam X-ray Topography (SWBXT) has been applied to the study of growth defects in SiGe/Si heterostructures. In the present study, a $15\mu\text{m}$ SiGe thin film grown on the (100) Si substrate is investigated. In Figure 1 (a), a transmission X-ray topograph recorded by using (040) reflection shows two sets of well defined misfit dislocations, D_1 and D_2 , running parallel to the $[011]$ and $[0\bar{1}1]$ directions, respectively. It is also observed that these dislocations are out of contrast when reflections with g vectors parallel to the dislocation line directions are used. By using the $g \cdot b = 0$ criterion, these misfit dislocations are determined to be of edge in character with Burgers vectors parallel to the $[01\bar{1}]$ and $[011]$ directions. To investigate the misfit dislocation depth distribution, section X-ray topography was also employed. Figure 1 (b) shows a section topograph recorded from the central region of the sample. A extensive dark region with a thickness of approximately $15\mu\text{m}$ from the top surface is observed. This area corresponds to the position of the SiGe epilayer. This observation strongly suggests that the as-grown thin film is highly strained. Moreover, irregular linear features (indicated by L) arising from severe lattice distortions in the region near to the surface layer were also observed. The development of a better understanding of the origin of the lattice distortions is needed to improve the crystalline quality of these as-grown SiGe thin films.

Figure 1.

* Acknowledgements: Work performed on the Synchrotron Topography Project, Beamline X-19C.

Figure 2.

Characterization of Growth Defects in THM grown HgCdTe Single Crystals by Using Synchrotron White Beam X-ray Topography *	X19C
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H. Chung, B. Raghoeamchar, and M. Dudley (SUNY Stony Brook), D. C. Gillies (NASA Marshall Space Flight Center)

Structural defects in Travelling Heater Method (THM) grown $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ single crystals have been investigated using Synchrotron White Beam X-ray Topography (SWBXT). Figure 1 shows an X-ray reflection topograph ($g=335$, $\lambda=0.82\text{\AA}$) recorded from a THM grown MCT sample. Defects such as small angle tilt boundaries (SB), inclusions (I), surface scratches (S) and a microcrack (C) were characterized. It is worth noting that no twins nor lattice distortions associated with inhomogeneous strain is observed. Our observations reveal that the MCT crystal exhibit a very high crystalline quality.

Figure 1.

* Acknowledgements: Work performed on the Synchrotron Topography Project, Beamline X-19C, and supported by NASA Marshall Space Flight Center under Grant No. NCC8-53.

Studies of Interface Demarcation and Structural Defects in Ga Doped Ge Single Crystals Using Synchrotron White Beam X-ray Topography *	X19C
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H. Chung, B. Raghoeamchar, and M. Dudley (SUNY Stony Brook), M. Lichtensteiger and D. C. Gillies (NASA Marshall Flight Center)

Synchrotron White Beam X-ray Topography (SWBXT) has been successfully applied to characterize marked growth interfaces in Ga doped Ge single crystals. The techniques employed in interface demarcation include modifications of cold zone temperature, mechanical pulsing and Peltier pulsing. As revealed by our observations, the visibility of a marked growth interface is a sensitive function of the diffraction conditions. A combination of the correct orientation of the active reciprocal lattice with respect to the interface plane and the necessary strain sensitivity controlled by the rocking curve width of the reflection proves to be the prerequisite for interface visibility. This prerequisite can easily be achieved by using synchrotron radiation since the tunability of the synchrotron source provides great flexibility in the choice of proper diffraction conditions. Moreover, the wide spectral range in the synchrotron source enables multiple topographic images to be recorded in a single exposure. Abundant information concerning defect structures in the crystal is also obtained. Figure 1 shows a topograph recorded from a Ga doped Ge crystal. Growth interfaces (I) induced by Peltier pulsing are clearly visible. Other defects such as small-angle tilt boundaries (SB), precipitates (P) and dislocation cell structures (C) were also observed. Direct evidence of dislocations present in the seed crystal propagating into the as-grown crystal through the melt-back interface during crystal growth was also obtained.

Figure 1.

* Acknowledgements: Work performed on the Synchrotron Topography Project, Beamline X-19C, and supported by NASA Marshall Space Flight Center under Grant No. NCC8-53.

Studies of Defect Structures in PVT grown CdZnTe single crystals
Using Synchrotron White Beam X-ray Topography *

X19C

H. Chung, B. Raghoeamachar, and M. Dudley (SUNY Stony Brook), W. Palosz and D.C. Gillies (NASA Marshall Space Center)

A (111) $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x=0.2$) sample cut from a boule grown by PVT method thinned down to the thickness of $200\mu\text{m}$ was characterized by using Synchrotron White Beam X-ray Topography (SWBXT). Figure 1 shows an X-ray topograph recorded in reflection geometry. Defects such as twins (T), precipitates (P), cracks (C) were observed. Two types of subgrain boundaries (SB_1 and SB_2) were also characterized. The first type comprise of dislocation cell structures with subgrains of 50 to $200\mu\text{m}$ in width. The second type, which are long and straight, run mainly parallel to the crystallographic $\langle 110 \rangle$ directions. The formation of dislocation cell structures is attributed to dislocation glide and climb caused by thermal-gradient-induced stresses generated during crystal growth. The second type can be formed by the polygonization of slip dislocations generated during the post-growth cooling process.[1,2] These observations indicate that thermal stresses induced during crystal growth and postgrowth cooling processes can play an important role in the development of defect structures in as-grown crystals.

[1] S. McDevitt, B. E. Dean, D. G. Ryding, F. J. Scheltens and S. Mahajan, Mater. Lett. 4, 11, (1986).

[2] K. Durose and G. J. Russell, J. Cryst. Growth, 86, 471 (1988).

Figure 1.

Synchrotron White Beam X-ray Topography Characterization of
Twin Structures in Vapor Grown CdZnTe Single Crystals *

X19C

H. Chung, B. Raghoeamachar, and M. Dudley (SUNY Stony Brook), W. Palosz and D.C. Gillies (NASA Marshall Space Flight Center)

CdZnTe which crystallizes in the sphalerite structure is prone to twinning. Twinning can occur through growth accidents resulting from fluctuations in growth rate and mechanical deformation such as wall contact. In this study, twin structures in PVT grown $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x=0.04$) single crystals have been studied in detail using Synchrotron White Beam X-ray Topography (SWBXT). Due to a high transport rate during sublimation, twins appear with higher probability in vapor grown crystals than in Bridgman grown material. Figure 1 is an X-ray topograph recorded in reflection geometry. Extensive twin structures comprising both large-volume macroscopic twins and thick twin lamellae, were observed. From detailed analysis of the Laue diffraction pattern recorded from these regions, one can determine that these regions are related to the matrix by a successive 180° rotation about the $[111]$ direction. Other defects such as slip bands (S), precipitates (P), cracks (C) and surface scratches (X) were also observed as shown in Figure 1. It is worth noting the irregular distributions of slip bands across twin boundaries indicating that the twinning process may have occurred earlier than the slip process and that the twin boundaries may act as barriers to dislocation motion. Similar phenomena were also observed in InP and ZnTe crystals. [1,2].

[1] S. Tohno and A. Katsui, J. Cryst. Growth, 74, 362 (1986).

[2] W. Zhou, M. Dudley, J. Wu, C. H. Su, M. P. Volz, D. C. Gillies, F. R. Sofron and S. L. Lehoczky, Mater. Sci. Eng. B27, 143, (1994).

Figure 1.

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* Acknowledgements: Work performed on the Synchrotron Topography Project, Beamline X-19C, and supported by NASA Marshall Space Flight Center under Grant No. NCC8-53.

Studies of Twinning in LEK Grown InP Single Crystals by Using Synchrotron White Beam X-ray Topography

X19C

H. Chung, W. Si, M. Dudley, and V. Prasad (SUNY Stony Brook), A. Anselmo and D.F. Bliss (US Air Force Rome Laboratory)

InP is the basic material for long wavelength optoelectronic devices. Its importance for high frequency devices also increases continuously. Their applications lead to an increasing demand for InP substrates of high crystalline quality, i.e., twin-free and low dislocation density. Extensive attention is paid to suppress the occurrence of twinning. However, due to a low stacking fault energy, InP crystals have a very strong tendency to twin. In spite of the growth twin-free crystals has been reported, it is still difficult to develop a set of growth conditions which can reproducibly produce twin-free crystals. In this report, Synchrotron White Beam X-ray Topography (SWBXT) has been applied to study twins in liquid encapsulated Kyropoulos (LEK) grown InP single crystals. Figure 1 is a highly magnified transmission X-ray topograph showing a long, thin twin lamella. From detailed analyses of the Laue diffraction patterns recorded from this region, one can determine that the twinned region is related to the matrix by a 180° rotation about the $[11\bar{1}]$ axis. The surface normal of the twin related region is parallel to the $[2\bar{2}1]$ direction. Figure 2 is a series of stereographic projections showing the twin operation.

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Figure 1.

Figure 2.

CHARACTERIZATION OF DEFECT STRUCTURES IN (111) 3C-SiC SINGLE CRYSTALS BY SYNCHROTRON TOPOGRAPHY *

X19C

W. Huang, M. Dudley (SUNY at SB); C. Fazi (Army Research Lab)

3C-SiC possesses high low-field electron mobility, which could potentially be exploited to produce devices and circuits for microwave power and other applications. However it is hard to obtain device quality 3C-SiC single crystals. Recently, synchrotron white beam x-ray topography has been used to study (111) 3C-SiC single crystals grown by a novel technique. Results show that the quality of these crystals is sufficiently good for device fabrication. Figure 1(a) is a transmission topograph recorded from a such crystal. Pendellosung fringes near the edges of the crystal, marked by P, indicate the high quality of the crystal. Major types of defects are found to be stacking faults on 111 planes, indicated by SF, inclusions, indicated by I, and dislocations, including growth dislocations and partial dislocations bounding stacking faults, indicated by GB and PB, respectively. Double positioning twins are also revealed, as shown in figure 1(b), which is recorded from the same crystal. From detailed analysis carried out using a combination of Nomarski interference microscopy and white beam x-ray topography in both transmission and reflection geometries, the double positioning twins are found to be in a layered configuration. This kind of structure decreases the influence of the double positioning boundary (DPB) on device performance and as such is tolerable.

Figure 1. Transmission synchrotron topographs recorded from (111) 3C-SiC crystal

* Acknowledgements: Work performed on the Synchrotron Topography Project Beamline X-19C, supported by U.S. Army Research Laboratory under grant No. DAAL02-92-R-9147/2FE425 and U.S. Army Research Office under grant numbers DAAH04-94-G-0091 and DAAH04-94-G-0121.

APPLICATION OF SYNCHROTRON WHITE BEAM MULTIPLE DIFFRACTION LINE ANALYSIS IN MEASUREMENT OF CURVATURE OF SINGLE CRYSTALS INDUCED BY LATTICE MISMATCH *

X19C

W. Huang, M. Dudley (SUNY at SB); J. Parsons (Oregon Graduate Institute); C. Fazi (Army Research Lab.)

Multiple diffraction lines appear in synchrotron x-ray topographs in bent crystals or epitaxially grown single crystals. These multiple diffraction lines can be interpreted according to the dynamical theory of x-ray diffraction as equal-inclination fringes. Since they are sensitive to small deformations in the crystal lattice, multiple diffraction line analysis can be used to measure the deformation field induced by bending or deposition of thin films. Figure 1(a) shows a transmission topograph recorded from a 6H-SiC wafer with 3C-SiC thin film grown on it. Since there is a lattice mismatch between the substrate and epilayer, residual stress exists in this wafer. Some narrow strips, or multiple diffraction lines which are indicated by arrowheads, with relatively lower intensity are visible. The position of the multiple diffraction lines changes when the crystal is rotated, as shown in figure 1(b). The movement of these lines as a function of crystal rotation represents the curvature of the crystal so that the deformation field can be calculated. Additional strain fields induced by inclusions, indicated by I, are also visible.

Figure 1.

* Acknowledgements: Work performed on the Synchrotron Topography Project Beamline X-19C, supported by U.S. Army Research Laboratory under grant No. DAAL02-92-R-9147/2FE425 and U.S. Army Research Office under grant numbers DAAH04-94-G-0091 and DAAH04-94-G-0121.

CHARACTERIZATION OF DEFORMATION IN SINGLE CRYSTALS BY SYNCHROTRON WHITE BEAM ABSORPTION EDGE CONTOUR MAPPING *

X19C

W. Huang, M. Dudley (SUNY at SB); J. Parsons (Oregon Graduate Institute); C. Fazi (Army Research lab.)

Residual stresses due to lattice mismatch between epitaxial layers and substrates can greatly affect the microelectronic performance of a device. Measurement of the curvature induced in a wafer by the stress in a thin film has long been used as a convenient and accurate technique for the determination of the deformation field. In this work, synchrotron white beam absorption edge contour mapping is employed to determine the curvature in a 6H-SiC wafer with a 3C-SiC epitaxial layer. Because of its high contour resolution and the high efficiency of data collection, this technique is considered to be superior to monochromatic x-ray contour mapping. A Mo filter, with an absorption edge at 0.618 Å, has been used so that there is an abrupt change in spectrum intensity. When the specimen is properly oriented with respect to the incident beam, a variation of observed contrast occurs when the range of diffract wavelengths span the absorption edge of the filter, forming an absorption edge contour. Upon rotation of the crystal a new crystal position will reflect at the absorption edge and a new contour appears, as shown in figures 1(a) through (d). Figure 1(e) shows an absorption edge contour map. The curvature of the specimen can be calculated by measuring the displacement of absorption edge contours as a function of rotation angle and the in plane strain field can be solved from several contour maps recorded in different diffraction conditions. This technique could potentially be used in the real time recording of stress formation and relaxation.

Figure 1.

* Acknowledgements: Work performed on the Synchrotron Topography Project Beamline X-19C, supported by U.S. Army Research Laboratory under grant No. DAAL02-92-R-9147/2FE425 and U.S. Army Research Office under grant numbers DAAH04-94-G-0091 and DAAH04-94-G-0121.

MEASUREMENT OF RESIDUAL STRESS IN SINGLE CRYSTALS BY SYNCHROTRON WHITE BEAM DIVERGENCE ANALYSIS *	X19C
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W. Huang, M. Dudley (SUNY Stony Brook); J. Parsons (Oregon Graduate Institute); C. Fazi (U.S. Army Research Lab.)

The deposition of epitaxial layers and metallization layers often induces residual stresses which may result in device failure. Therefore the characterization of stress and strain fields in thin films and substrates is important in device fabrication. Synchrotron white beam topography, which is commonly used to image individual defects and defect distributions, can also be used in quantitative Bragg angle mapping. This technique has been used to measure the stress and strain fields in 6H-SiC single crystals with 3C-SiC thin films grown on them. Figure 1(a) shows transmission diffraction images recorded from the crystal with the film at x-ray exit surface and figure 1(b) shows the quantitative Bragg angle map. Figure 1(b) was recorded by multi-exposure using an x-ray beam of 0.5mm by 5mm in size to image different positions in the crystal. The Bragg angle of each intersection of diffracted lines can be measured. Larger film-specimen distance leads to higher measurement accuracy. Since there is a non-uniform deformation field in the crystal, the variation in Bragg angles is visible. The deformation in the film covered area is different from that in the film free area. A combination of white beam absorption edge contour mapping and quantitative Bragg angle mapping allows the residual stress and strain field to be calculated. An accuracy in $\Delta d / d$ of 10^{-3} can be achieved.

Figure 1.

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OBSERVATION OF DISLOCATION CONTRAST REVERSAL INDUCED BY STRAIN FIELD *	X19C
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W. Huang, M. Dudley (SUNY at SBB); J. Parsons (Oregon Graduate Institute); C. Fazi (Army Research Lab.)

Synchrotron white beam x-ray topography has been used to study 6H-SiC wafers with 3C thin films grown on them. Figure 1(a) is a reflection topograph recorded from a such wafer. The penetration depth is large enough to reveal information from both film and substrate. It shows that the contrast from dislocations in the film-covered region is different from that in film-free regions. The same phenomenon can be observed in the transmission topograph shown in figure 1(b). Close observation of the boundary between the film-covered and film-free regions shows that the overall diffracted intensity from the film-covered area was enhanced. These area contrast differences may be attributed to the substrate strain field associated with the thin film. The diffracted intensity from the film-free region was near the value calculated for a perfect crystal, and it increased with the lattice strain up to almost the value calculated for an "ideally imperfect" crystal, for which the diffracted intensity is proportional to Fh^2 instead of Fh . The intensity of the dislocations is between these values so that the dislocations appear to be dark in the film-free region and light in the film-covered region. This means that the thin film region is highly strained.

This result has been proved by the measurement of rocking curve widths of film area and substrate area. The rocking curve width of the film region is much larger than the theoretical perfect crystal value.

Figure 1. (a) Synchrotron reflection topograph and (b) transmission topograph showing dislocation contrast reversal.

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Ning Lei, Zhengqing Huang and Stuart A. Rice (U. of Chicago)

The atomic density distribution normal to the liquid-vapor interface of a bismuth: gallium mixture (0.18% Bi and 99.82% Ga in mole) has been studied by the measurement of the x-ray specular reflection in the range of $q_z \in [0.3, 2.6 \text{ \AA}^{-1}]$. The reflection curve, measured at temperature $\sim 25^\circ\text{C}$, after division by the theoretical Fresnel reflectivity factor for gallium, is shown as circles in Fig. a. We can fit the data very well to a complete bismuth monolayer on top of bulk liquid gallium, and the fit is shown in solid line in the figure. The vertical atomic density profile obtained from the fit is shown in Fig. b. Besides the reflection measurements, our in-plane data show that there is a bismuth liquid peak plus liquid gallium scattering, and thus reproduce the data obtained earlier by our group. Measurements have been carried out at three temperatures. Our current work is on the surface structure in the gallium:tin alloy system.

Figure 1. (Left) Circles denote the experimentally obtained specular reflection after divided by the theoretical Fresnel reflectivity for gallium. The solid line denotes the fit to a complete bismuth monolayer on top of bulk of liquid gallium. (Right) The atomic distribution to the interface, obtained from the fit.

B. Lin, M. Meron, P. J. Viccaro (U of Chicago), M. L. Schlossman, S. Williams (U of IL, Chicago)

X-ray beams of varying degrees of partial spatial coherence have been prepared and characterized by using two slits, and the diffraction of these beams from optical gratings have been measured. The experiments were carried out at a bending magnet source at the NSLS (X-19C). The resulting diffraction patterns for optical gratings are analyzed in terms of an x-ray mutual coherence function, used to describe the propagation of the coherent wavefront in the visible light regime. The diffraction and speckle pattern from the surface are the result of the mutual coherence function describing the degree of partial coherence of the beam convoluted with the interference function of the grating. We show that the speckle patterns formed from partially coherent wavefronts contain relevant information concerning the interference function characterizing the grating surface.

Forming diffraction patterns, or x-ray speckles, with partially coherent x-rays as a probe of the surface relaxes the requirement for the interference, therefore gaining in the "effective" coherent flux. In addition, detailed knowledge on the propagation of the spatial coherence of x-rays aids in defining the physical characteristics of optical elements in the beamline which must preserve the coherence wave front of x-rays.

Figure 1. Fraunhofer diffraction patterns measured from two vertical slits; the first slit is 3.5 meter upstream of the second slit. The size of the second slit was varied from 0.5 microns to 20 microns while the first slit was fixed at 50 microns. The solid lines are fits of data (represented by the diamonds) to an intensity function which is the Fourier transform of the coherence function (shown in Fig. 1) multiplied by the autocorrelation function of the second slit.

Figure 2. The mutual coherence function defined by the two slits depicted in Fig. 1; it describe the degree of partial (spatial) coherence as a function the second slit with the first slit fixed.

Characterization of structural defects in ZnSe by synchrotron white beam x-ray topography *

X19C

B. Raghathamachar, H. Chung, M. Dudley, (SUNY at Stony Brook), B. Fitzpatrick (Optical Semiconductors, Inc.)

ZnSe is an important II-VI semiconductor possessing a large direct energy band gap and therefore, good electroluminescence which makes it a candidate material for light emitting diodes and lasers. However, defects such as dislocations, twins, subgrain boundaries, etc. which can be routinely introduced in the crystal during growth can be potentially detrimental to device performance. Hence, identification and characterization of defect structures in this material is of paramount importance. Synchrotron white beam x-ray topography has been used to study structural defects in ZnSe crystals. Figure 1 shows a reflection topograph taken from a ZnSe single crystal grain. In the lower regions of the figure, we can see several white bands which are actually regions of zero intensity caused by orientation contrast. This occurs because of the presence of several microtwins. Microtwinning occurs at the high growth temperatures used, due to the small differences of free energy between zinc blend and wurtzite structures, and temperature fluctuations. Continuous phase transformation between these two structures results in change in the stacking sequence in the [111] direction leading to twinning. Figure 1 also reveals bands of zero intensity running across the microtwins. This orientation contrast is associated with subgrain boundaries which are formed during post growth cooling as a result of polygonization of dislocations. Upper parts of the figure reveal distortion which is associated with inhomogeneous strain associated with a distorted lattice. This could again be due to temperature fluctuations.

Figure 1. Reflection topograph from a ZnSe single crystal grain showing microtwinning (T), subgrain boundaries (SB) and lattice distortion (A).

* Work performed on the Synchrotron Topography Project, Beamline X19C.

Studies on the influence of post solidification cooling rate on the crystalline perfection of CdZnTe single crystals by synchrotron white beam x-ray topography *

X19C

B. Raghathamachar, H. Chung, M. Dudley, D. J. Larson Jr. (SUNY at Stony Brook)

CdZnTe single crystals grown by the seeded Bridgman method in a microgravity environment aboard space shuttle flight USML-1 were examined by synchrotron white beam x-ray topography. The microgravity environment is expected to improve crystalline perfection because of the absence of hydrostatic forces and gravity driven convection. After growth, the CdZnTe boule was subjected to accelerated post solidification cooling down its length. Wafers sliced from regions cooled at different cooling rates were examined by transmission topography. Figure 1(a) shows a transmission topograph recorded from a region cooled with a low cooling rate. The image shows the very low dislocation density, with individual dislocations (D) capable of being resolved. The singular dark spots are Te precipitates (P) while the straight lines lying parallel to the $[110]$ directions are characterized as lamellar 180° rotation twins (T) about the $[11\bar{1}]$ plane normal. Figure 1(b) shows a topograph recorded from a more rapidly cooled region of the boule. It is obvious that this region exhibits a relatively higher dislocation density in addition to the presence of extremely fine Te precipitates. Due to the retrograde solubility of Te in solid CdZnTe, supersaturation of Te results in precipitation during cooling. Clearly the dislocation density as well as the size and density of Te precipitates are strongly influenced by the cooling rate. In conclusion, higher cooling rates are deleterious to the crystalline perfection of CdZnTe single crystals.

Figure 1. Transmission topographs ($g = \bar{1}\bar{1}3$, $\lambda = 0.42 \text{ \AA}$) recorded from different regions of a wafer sliced from a CdZnTe boule (a) from a slowly cooled region of the boule showing individual dislocations (D) and precipitates (P) and (b) from a rapidly cooled region of the boule.

* Work performed on the Synchrotron Topography Project, Beamline X19C and supported by NASA Marshall Space Flight Center.

Surface topography studies of an as-grown boule of CdZnTe *

X19C

B. Raghothamachar, H. Chung, M. Dudley, D.J. Larson Jr.(SUNY at Stony Brook)

Synchrotron white beam x-ray topography was used to study the surface of an as-grown CdZnTe boule(GCRC-1) grown in a quartz ampoule by the seeded Bridgman-Stockbarger method of crystal growth in a microgravity environment aboard space shuttle flight USML-1. Topography of the surface of the as grown boule, before cutting enables one to observe the true microstructure developed during the growth process, with no possibility of artifacts, for example due to polishing or cutting, to exist. In addition, effects due to thermal mismatch associated with rapid cooling as well as due to ampoule contact are likely to give rise to deformation microstructures concentrated near the periphery of the boule which is precisely the volume examined in surface topography studies. A reflection topographic image taken from the surface of the GCRC-1 boule is shown in Figure 1. Detailed examination of this image revealed extensive slip band networks(S) as well as high levels of surface strains in those regions that were in partial or full contact with the ampoule. Twins(T) appear to nucleate at regions of partial wall contact. Regions of no wall contact show a low defect density with little or no surface strain. Thermal stresses arising from rapid cooling as well due to ampoule wall contact are found to be the causes for these defect microstructures. Thus, surface topography of the boule is important in correlating the as grown deformation microstructure to the growth conditions.

Figure 1. Reflection topograph recorded from the outer surface of GCRC-1 boule showing twins (T) and slip bands (S).

* Work performed on the Synchrotron Topography Project, Beamline X19C and supported by NASA Marshall Space Flight Center.

Synchrotron x-ray topographic studies on the causes and nature of twinning in CdZnTe crystals *

X19C

B. Raghothamachar, H. Chung, M. Dudley, D.J. Larson, Jr.(SUNY at Stony Brook)

Synchrotron white beam x-ray topography has been used to characterise twinning in CdZnTe crystals. A wafer sliced from a CdZnTe boule grown by the seeded Bridgman-Stockbarger method in a microgravity environment was used for our studies. Figure 1 (a) shows a synchrotron white beam x-ray reflection topograph which easily reveals the matrix and twinned regions by orientation contrast. Correlating the position of the wafer to the overall boule microstructure, it was found that the twin T_1 nucleated from the shoulder region of the boule where a bubble is present. This clearly indicates that the nucleation of the twin occurred during growth due to disturbances at the growth interface caused by the changing diameter of the shoulder as well as the presence of the bubble. Figure 1(b) and (c) show Laue back reflection topographs recorded from the matrix and twinned region (T_1) respectively, showing the orientations of these two regions. The twinned region is related to the matrix by a 180° rotation about the $[111]$ axis. Similarly, the twinned region T_2 is related to the matrix by 180° rotation about the $[\bar{1}11]$ axis. Stress caused by ampoule wall contact could be the possible cause for the nucleation of twin T_2 .

Figure 1. (a)Synchrotron white beam x-ray topograph ($g = 133$, $\lambda = 0.98 \text{ \AA}$) showing twin related regions T_1 and T_2 revealed by orientation contrast. Laue back reflection patterns recorded from (b)matrix and (c)twinned region T_1 show that the twinned regions are related to the matrix by a 180° rotation about the $[111]$ axis.

* Work performed on the Synchrotron Topography Project, Beamline X19C and supported by NASA Marshall Space Flight Center.

Synchrotron x-ray topography studies of formation of slip bands and subgrain boundaries in Bridgman grown CdZnTe single crystals *

X19C

B. Raghothamachar, H. Chung, M. Dudley, D.J. Larson Jr.(SUNY at Stony Brook)

Wafers sliced from a microgravity grown CdZnTe boule(GCRC-1) were studied by synchrotron white beam x-ray topography. The reflection topograph shown in Figure 1(a) taken from a wafer(#4) sliced from the middle of the boule, reveals two sets of lines running along the $[1\bar{1}0]$ and the $[0\bar{1}1]$ directions. These are slip band networks which are initiated at the peripheral regions and extend into the interior. By analyzing projected directions in different reflections, the slip bands S_1 and S_2 can be characterized as belonging to the $[10\bar{1}]/(\bar{1}11)$ and $[0\bar{1}1]/(\bar{1}11)$ slip systems respectively. These slip bands are generated from the distorted region A_1 caused due to stress by wall contact. A reflection topograph (Fig. 1(b)) recorded from a wafer(#7) further down the boule shows, by orientation contrast, two sets of long and straight sub-grain boundaries running parallel to the $[1\bar{1}0]$ (SB_1) and $[0\bar{1}1]$ (SB_2) directions respectively from the periphery to the interior. The overlapping or separation of the images is attributed to the different senses of tilt between neighboring subgrains. During cool-down, dislocations undergo polygonization which involves dislocation movement by gliding and climbing to form energetically stable configurations of subgrain boundaries accommodating tilt orientation.

Figure 1. (a)Reflection topograph from GCRC-1 wafer # 4 ($g = 404$, $\lambda = 0.98\text{\AA}$), showing the slip bands S_1 and S_2 . (b)Reflection topograph from GCRC-1 wafer # 7 ($g = 044$, $\lambda = 0.76\text{\AA}$) showing sub-grain boundaries SB_1 and SB_2 .

* Work performed on the Synchrotron Topography Project, Beamline X19C and supported by NASA Marshall Space Flight Center.

The Application of Synchrotron X-Ray Radiation to the Development of Time Resolved Methods for the Study of RNA Folding

X19C

B. Sclavi, M. Sullivan, M. Chance, M. Brenowitz (Albert Einstein College of Medicine), and S. Woodson (Univ. of Maryland)

The radiolysis of water by high energy x-rays produces free electrons and hydroxyl radicals. Hydroxyl radicals, which can break the phosphodiester backbone of DNA and RNA, have proven to be valuable reagents in the study of nucleic acid structure and protein-nucleic acid interactions. Irradiation of solutions containing ^{32}P labeled RNA by a high flux "white light" x-ray beam, X19C at NSLS, yields sufficient concentrations of hydroxyl radicals so that folding studies can be conducted with single basepair resolution at millisecond timescales. Preliminary studies of the Mg^{2+} dependent folding of the Tetrahymena Sca I ribozyme are presented. This synchrotron based technology is a novel method with which to examine the time-resolved structural changes of nucleic acid conformation and protein-nucleic acid complexes.

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Applications of absorption edge contour (AEC) mapping in Fe doped InP single crystal wafers *	X19C
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W. Si, H. Chung, M. Dudley, and V. Prasad (SUNY Stony Brook), A. Anselmo and D. F. Bliss (USAF Rome Laboratory)

Among synchrotron white beam x-ray topography techniques, AEC mapping is a unique technique which can accurately determine the strain field distribution in a single crystal sample. It is based on the principle that when a deformed single crystal is irradiated by a white beam of synchrotron radiation, different areas of the crystal will diffract different wavelengths of x-rays available in the continuous spectrum of the incident beam. A significant variation of observed contrast occurs when the range of diffracted wavelengths spans the absorption edge (λ_{edge}) of the specimen or of a suitably chosen filter material which is inserted in the path of the beam. If an orientation is chosen such that a certain area of the sample will reflect wavelengths below that of the edge, the diffraction intensity will be correspondingly greatly attenuated; while in the other area of the sample, which reflects wavelengths above that of the edge, the diffracted intensity is only slightly modified. Upon rotation of the crystal by a known amount about a known axis, the positions which were diffracting at λ_{edge} will select a new wavelength and consequently a new position will diffract at λ_{edge} . In this way the distortion field in the crystal can be mapped. Preliminary results obtained from an Fe doped InP wafer are shown in Fig. 1, where $g = 022$, $\lambda_{edge} = 0.44371 \text{ \AA}$, $\theta_B = 6.138^\circ$. In the figure, the frame denotes the incident beam size, and the absorption edge sweeps across the sample as the crystal rotates through 0.02° steps. The sensitivity, $(\Delta d/d)$, here is of the order of one part in 10^3 .

Figure 1.

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Investigation of defect structures in Sn doped InP single crystals by synchrotron x-ray transmission topography *	X19C
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W. Si, H. Chung, M. Dudley, and V. Prasad (SUNY Stony Brook), A. Anselmo and D. F. Bliss (USAF Rome Laboratory)

Large size InP single crystals (Sn doped, concentration: 5.90×10^{18} atoms/cc) were grown by a high pressure, in-situ synthesis technique. (110) wafers ($\sim 40 \times 70 \times 1 \text{ mm}^3$) were cut from the [001] axis grown boule. Transmission geometries were adopted to characterize the defect structures in the crystals. Figure 1 shows transmission topographs, $g = \bar{2}20$, $\lambda = 0.51 \text{ \AA}$, which shows (a) precipitates (P) and dislocations (D), and (b) a micro-twin lamella (T). The absorption condition here is $\mu t = 4.4$, with $\lambda = 0.51 \text{ \AA}$, linear absorption coefficient $\mu = 44.3 \text{ 1/cm}$, and thickness $t = 0.1 \text{ cm}$. Under such high absorption conditions, precipitates exhibit two-lobe black-white contrast, with the dark lobe on the side of positive g . This indicates that the lattice of the matrix around the precipitate is under tension. The micro-twin lamella (about $10 \text{ }\mu\text{m}$ in width) is a 180° rotation twin ($\pm(111)$ twin planes). This long thin twin lamella originating from the seed, runs through the whole wafer, reiterating the importance of the examination of the seed crystal before crystal growth.

Figure 1.

* Acknowledgments: Research carried out under auspices of the ARPA/AFOSR Consortium of Crystal Growth Research (Contract No. F496209510407), work performed on the Synchrotron Topography Project, Beamline X-19C.

Study of defect distributions in S doped InP single crystals by synchrotron x-ray reflection topography *

X19C

W. Si, H. Chung, M. Dudley, and V. Prasad (SUNY Stony Brook), A. Anselmo and D. F. Bliss (USAF Rome Laboratory)

High quality InP single crystals (S doped, concentration: 3.90×10^{19} atoms/cc) were grown by a high pressure, in-situ one-step synthesis technique. (110) wafers ($\sim 40 \times 60 \text{ mm}^2$ in size, 1 mm thick) were sliced from the single crystal boule, with [001] as the pulling direction. For the synchrotron white beam x-ray topography, reflection geometries were adopted to characterize the defect distributions in the crystals. Both slip bands and growth striations were revealed. Figure 1 shows reflection topographs of a S-doped InP single crystal, $g = 440$, $\lambda = 0.74 \text{ \AA}$, which reveals (a) slip bands (SB), and (b) growth striations (GS). Most slip bands were generated from the shoulder region of the boule, indicating that stress is concentrated in this region. There are two sets of slip planes, $\pm(\bar{1}11)$ and $\pm(1\bar{1}1)$. The traces of the intersection of $\pm(\bar{1}11)$ and $\pm(1\bar{1}1)$ with sample surface plane (110) are $\pm[\bar{1}12]$ and $\pm[1\bar{1}2]$ directions, respectively. Growth striations which are convex to the melt were found in some areas. The shape of the growth striation reveals the shape of the solid-liquid interface during crystal solidification, which can provide some useful information for the thermal modeling of the crystal growth process.

Figure 1.

* Acknowledgments: Research carried out under auspices of the ARPA/AFOSR Consortium of Crystal Growth Research (Contract No. F496209510407), work performed on the Synchrotron Topography Project, Beamline X-19C.

Study of effect of magnetic field on Fe precipitates in Fe-doped InP single crystals using synchrotron white beam x-ray topography *

X19C

W. Si, H. Chung, M. Dudley, and V. Prasad (SUNY Stony Brook), A. Anselmo and D. F. Bliss (USAF Rome Laboratory)

Semi-insulating Fe-doped InP is an ideal material for long wavelength optoelectronic devices and high frequency electronic devices. In the present study, high concentration Fe-doped InP single crystals have been grown using the magnetic liquid encapsulated Kyropoulos (MLEK) method [1]. The effect of applied magnetic field on Fe precipitates formed in InP single crystals was investigated. A (110) plane cut wafer (about 0.5 mm thick) was sliced from the [001] grown single crystal boule. Figure 1 is a synchrotron white beam x-ray reflection topograph of the wafer, $g = 440$, $\lambda = 0.74 \text{ \AA}$, which shows slip bands (S), precipitates (P), and dislocation segments (D). The images of precipitates consist of two lobes separated by a line of no contrast which is perpendicular to the diffraction vector. This indicates the radial strain field associated with the precipitates. It is evident that at the areas where the magnetic field is turned off, there are a few large Fe precipitates, while at other areas where the magnetic field is turned on, there is no Fe precipitates visible on the topograph. This clearly indicates that the magnetic field greatly enhances the uniformity of the Fe dopant distribution.

[1]. D. F. Bliss et al, J. Crystal Growth, 128 (1993) 451-456.

Figure 1.

* Acknowledgments: Research carried out under auspices of the ARPA/AFOSR Consortium of Crystal Growth Research (Contract No. F496209510407), work performed on the Synchrotron Topography Project, Beamline X-19C.

Examination of high quality 4H-SiC single crystal wafers by synchrotron white beam x-ray transmission topography *	X19C
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W. Si and M. Dudley (SUNY Stony Brook), C. H. Carter, Jr. (Cree Research, Inc.)

SiC is a promising wide band-gap semiconductor material for advanced devices, owing to its excellent properties such as high breakdown field and high electron saturation drift velocity. Currently both 6H-SiC and 4H-SiC wafers (up to 30 mm in diameter) are commercially available, but recent emphasis has shifted to the 4H-SiC because of large electron mobility (800 vs. 370 cm²/V-s) and low donor activity energy (45 vs. 90 meV) of 4H-SiC compared to 6H-SiC. In the present work, a (0001) plane cut wafer grown by PVT method was characterized using synchrotron white beam x-ray topography. Figure 1 is a transmission topograph of typical good quality region of the wafer, $g = 0\bar{1}10$, $\lambda = 0.74 \text{ \AA}$. Various defect configurations were revealed, such as basal plane dislocations (BD), superscrew dislocations (SS), and scratches (SC). The line directions of the individual basal plane dislocation numbered 1 and 2 (upper right part of Figure 1) are $[\bar{1}\bar{1}20]$ and $[1\bar{2}10]$, respectively. These dislocations are all $1/3\langle 11\bar{2}0 \rangle / (0001)$ type perfect dislocations with primarily screw character [1]. In region A, the basal plane dislocation density is less than 100/cm², and no micropipes are observed, while in region E, the basal plane dislocation density is less than 1000 /cm², and again no micropipes are observed. Total number of micropipes in the whole field of view is 20, so that the micropipe density is around 12/cm². The abundance of residual scratches over the wafer surface indicates an improper polishing process. [1]. W. Huang, et al. in Applications of Synchrotron Radiation Techniques to Materials Science II, L. J. Terminello et al, (Eds.) MRS Symp. Proc. 375, 313, 1995.

Figure 1.

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Observation of 3C-SiC inclusions in 4H-SiC epitaxial films grown on 4H-SiC single crystal substrates *	X19C
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W. Si, W. Huang, and M. Dudley (SUNY Stony Brook), H. S. Kong and C. H. Carter, Jr. (Cree Research, Inc.)

During the epitaxial growth of 4H-SiC films on 4H-SiC single crystal substrates, 3C-SiC inclusions often occur in the epilayers. In the present study, SiC substrates were Si-face vicinal (0001) wafers with tilt angles of 3.5° towards the $[11\bar{2}0]$ directions. Since epilayer thicknesses were about 7 μm, the grazing incidence Bragg-Laue reflection geometry was employed. Figure 1(a) shows the diffraction pattern in parallel-recording setup (the wafer surface almost parallel to the x-ray film), with the $[1\bar{1}0]$ direction close being parallel to the incident beam. In the pictures, besides the 4H-SiC pattern, there are additional spots corresponding to the two different 3C-SiC structures. By indexing the pattern, there are two kinds of epitaxial relationships between 3C and 4H-SiC: for the 3C(I)-SiC, $(0001)_h // (111)_c$, $[10\bar{1}0]_h // [2\bar{1}\bar{1}]_c$; for the 3C(II)-SiC, $(0001)_h // (111)_c$, $[10\bar{1}0]_h // [\bar{2}11]_c$. This is due to the fact that the stacking sequence of 4H-SiC is ABAC and there are two possible configurations of 3C-SiC grown on it, those with ABCABC or ACBACB stacking sequences. Figure 1(b) is the enlargement of right part of Figure 1(a), showing more details of those 3C-SiC inclusions which usually exhibit as triangular shapes. The diffraction conditions are: $g = (113)3C(II)$, $\lambda = 0.67 \text{ \AA}$; $g = (220)3C(I)$, $\lambda = 0.91 \text{ \AA}$; $g = (017)$, $\lambda = 0.62 \text{ \AA}$; $g = (016)$, $\lambda = 0.78 \text{ \AA}$; $g = (015)$, $\lambda = 0.99 \text{ \AA}$. Further work on the correlation of topographs with Nomarski optical micrographs is being undertaken.

Figure 1.

* Acknowledgments: Work performed on the Synchrotron Topography Project, Beamline X-19C, and supported by ARPA/AFOSR under Grant No. FY1457-95-03108 through Cree Research, Inc. under Grant No. 95-004.

Determination of Burgers vectors of screw dislocations in 6H-SiC single crystals: I. Projection topography *

X19C

W. Si, S. Wang, and M. Dudley (SUNY Stony Brook), C. H. Carter, Jr. (Cree Research, Inc.)

Individual superscrew dislocations in 6H-SiC have been characterized using synchrotron white beam x-ray topography. The magnitude of the Burgers vector was determined from the magnitude of the tilt of the lattice planes on both sides of the dislocation core measured from projection topographs. This simple method can be illustrated as follows: the lattice tilt, ϕ , around the screw dislocation, at distance r from the dislocation core, can be described by: $\phi = b/2\pi r$, where b is the magnitude of Burgers vector. In projection topographs ($h = 0006$, $\lambda = 0.89 \text{ \AA}$) such as those shown in Figs. 1(a) and 1(b), this lattice tilt manifests itself in the form of a mutual longitudinal shift, S , of the two parallel components of the bimodal dislocation images (black lines) which is observable at the outcrop of the dislocations on the as-grown surface. By changing the sample-to-film distance D_{sf} , ϕ can be determined from the slope k of the linear S vs. D_{sf} plot (where $k = 4\phi$) which is shown in Fig. 1(c). Since the superscrew dislocations always have groups of basal plane dislocations attached to them, and these basal plane dislocations have edge components, the bimodal image width of the superscrew dislocations diverges as D_{sf} increases. In order to obtain the value of r corresponding to the measured tilt angle, ϕ , the width of the bimodal image is plotted as a function of D_{sf} as shown in Fig. 1(d). The image width, W_0 , at $D_{sf} = 0$, obtained by extrapolation, corresponds to $2r$. This enables the magnitude of the Burgers vector to be determined from the equation: $b = \pi W_0 k/4$. For the dislocation shown in Figures 1(a)-(d), the Burgers vector magnitude was found to be $52.6 \text{ \AA}$, corresponding to $3-4c$ (where c is the lattice constant along $[0001]$ axis, $c = 15.17 \text{ \AA}$), and the sense is left-handed.

* Work performed on the Synchrotron Topography Project, Beamline X-19C, and supported by ARPA/AFOSR under Grant No. FY1457-95-03108 through Cree Research, Inc. under Grant No. 95-004.

Determination of Burgers vectors of screw dislocations in 6H-SiC single crystals: II. Section topography *

X19C

W. Si, S. Wang, and M. Dudley (SUNY Stony Brook), C. H. Carter, Jr. (Cree Research Inc.)

A white-beam section topograph geometry has been used to measure the magnitude of the Burgers vector of superscrew dislocations in the 6H-SiC single crystals. This method consists of illuminating the sample by a strip of highly collimating white beam (less than $20 \text{ \mu m}$). Section topographs were taken in symmetric transmission, i.e., using Bragg planes perpendicular to the thin crystal platelet and perpendicular to the screw dislocation. In such cases the lattice tilts are easily derived from the linear displacements of Bragg diffracted beams. In principle, the lattice tilt T around the screw dislocation can be described as: $T = b/2\pi r$, where b is the magnitude of Burgers vector, r is the distance from the dislocation core. As to the white beam diffraction geometry, the deviation of Bragg angle $\Delta\theta_B$ would be $2T$. Assuming the incident beam is strictly parallel, the displacement Y recorded in the x-ray film at sample-to-film distance D_{sf} would be: $Y \cong D_{sf}\Delta\theta_B$ ($\Delta\theta_B$ is very small) $= 2D_{sf}T$, thus $b = \pi Yr/D_{sf}$. Figure 1 shows the lattice tilt T around a screw dislocation, and Figure 2 shows a white beam section topograph of a screw dislocation, $D_{sf} = 16 \text{ cm}$, $g = 0006$, $\lambda = 0.89 \text{ \AA}$. From the hyperbolae drawn on the pictures, the magnitude of the Burgers vector is $62.6 \text{ \AA}$ (upper left lobe), and $45.0 \text{ \AA}$ (lower right lobe), which again corresponds to $3c$ to $4c$ (c is the lattice constant along $[0001]$ axis, $c = 15.17 \text{ \AA}$).

Figure 1.

* Acknowledgments: Work performed on the Synchrotron Topography Project, Beamline X-19C, and supported by ARPA/AFOSR under Grant No. FY1457-95-03108 through Cree Research, Inc. under Grant No. 95-004.

Figure 2.

Observation of growth defects in GaInSb single crystal by synchrotron white beam x-ray topography

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GaInSb single crystals with $\langle 111 \rangle$ growth axes have been studied by SWBXT, the special solid-liquid growth interfaces have been revealed in Figure 1. Unlike crystals with other growth axes, the interface of GaInSb crystal with $\langle 111 \rangle$ growth direction developed a core region in the center. This is believed to be the $\{111\}$ plane. At the periphery, the interface was the normal convex curves. As shown in Figure 1, the lateral extent of the core increases at the end of growth processing, and the boundary of the core becomes much rougher. This is caused by Indium composition. During growth processing, Indium was continuously rejected into the melt from the solid-liquid interface so that there was a higher Indium content at the end of growth, which can be shown in Figure 2. This means a higher degree of supercooling was needed to solidify. The growth rate, therefore, became slower at the end, this led to the increased extent of $\{111\}$ facets. Indium concentration was measured in transverse direction in Figure 3, it clearly shows the core region has highest Indium concentration.

Work performed on Synchrotron Topography Project Beamline X-19C, and supported by Johnson Matthey Electronics.

Figure 1. Reflection topograph of the longitudinally cut GaInSb single crystal, $g=(112) \lambda=0.52 \text{ \AA}$

Figure 2. Indium content distribution along growth direction.

Synchrotron white beam x-ray topographic investigation of growth processing in GaInAs single crystal *

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GaInAs bulk crystal grown in $\langle 100 \rangle$ has been investigated by SWBXT. Using Figure 1 is an enlargement taken from this whole crystal image, where the growth striations clearly delineate the interface shape. These striations were formed due to periodic changes of Indium concentration. Such small disorders in Indium concentration may lead to the change of growth rate and perturb the solid-liquid interface, and more seriously it can break the thermal equilibrium at interface and lead to generate growth defects. In Figure 1, the onset of interface breakdown was clearly revealed, the unstable convex interface undergoes sinusoidal perturbations (P) and eventually breaks down (the dark region). Dislocations (D) are observed to end or nucleate from this region. Figure 2 also shows a region of cellular growth (C).

Figure 1. High magnification of reflection topograph recorded from a GaInAs single crystal, $g=(022) \lambda=0.84$.

Figure 2. Reflection topograph obtaining a cellular structure. $g=(022) \lambda=0.84 \text{ \AA}$.

* Work performed on Synchrotron Topography Project Beamline X-19C, and supported by Johnson Matthey Electronics.

Studies of quartz crystal bars using synchrotron white beam x-ray topography *

X19C

J. Su, M. Dudley (SUNY Stony Brook), T. McLelland, B. Goldfrank (Frequency Electronics Inc.)

Quartz crystal (α -quartz) resonators are an important part of modern communication and satellite navigation systems. Defects in these crystals can introduce detrimental frequency offsets. The sweeping process, which is electric-field driven, solid-state diffusion at elevated temperature, is applied to purify the crystals. X-ray reflection topography has been used to study the defects in swept synthetic quartz crystal bars which are used to make high precision SC cut quartz resonators. The bars are of X and Z surface orientations, and have dimensions of 182mm $\times$ 18mm $\times$ 15mm. Figure 1 shows reflection topographs of -X and -Z surfaces from one of bars. On the -X surface, dislocations (D) are clearly observed, some dislocations end at surface. In the -Z surface, the emergent ends of dislocations which may be decorated with impurities are revealed, also sweeping induced impurity accumulations (IA) are visible on the surface. From the distribution of dislocation outcrops and their associated strains on the -X surface, it can be determined that the dislocations are nearly parallel to Z axis.

Figure 1. Reflection topographs of -x and -Z surfaces from quartz bar K064-1,

* Work performed on Synchrotron Topography Project: Beamline X19C, and supported by Frequency Electronics Inc.

Comparison of quartz resonator bonding strain by synchrotron white beam topography *

X19C

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Manufacturing induced defects play an important role in quartz resonator device yield. Bonding strain can be extremely deleterious to resonator performance. SWBXT is a non-invasive technique which is very suitable for the study of such defect distributions. Samples with different bonding process have been studied by SWBXT, those which have thermal compression (TC) bonding and those which have undergone epoxy bonding. Figures 1 and 2 show the reflection topographs of a resonator with TC bonding and a resonator with epoxy bonding. The bonding strain (S) is nearly invisible in Figure 1, but, in Figure 2, the bonding process induced larger strain fields (S) at the resonator periphery, and some strain field even extends into the central region, where is the active oscillating area of a precision resonator. This will inevitably influence the resonator performance. This work clearly shows that epoxy bonding process creates more strain than the TC bonding process. Dislocations (D) and electrode induced strain fields (ES) are revealed in the Figures.

Figure 1. Reflection topograph of a resonator with TC bonding.

* Work performed on Synchrotron Topography Project: Beamline X-19C, supported by Frequency Electronics Inc.

Figure 2. Reflection topograph of a resonator with epoxy bonding.

X-Ray Topography and Fluorescence Microscopy of a Basal Cut 6H-SiC Wafer *	X19C
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W. M. Vetter, M. Dudley (SUNY at Stony Brook).

Super screw dislocations are the primary defect in commercial PVT 6H-SiC single crystal wafers. Those with the largest Burgers vectors typically have optically visible cylindrical voids or "micropipes," coinciding with their dislocation cores. A basal-cut 6H-SiC sample was impregnated with fluorescent epoxy, staining its voids. Figures 1 and 2 show SWBXT images recorded in back-reflection and transmission geometries, respectively. The main features observable in figure 1, ($g=(00024)$, $\lambda=1.25\text{\AA}$), consist of black rings with white centers of various diameters that are associated with the surface intersections of superscrew dislocations of various sized Burgers vectors (b). In addition to the larger Burgers vector superscrew dislocations (greater than about $b=3c$) that are associated with micropipes, indicated by P, there are many smaller circular features, p, that have no corresponding micropipes observable by fluorescence microscopy. Figure 2 ($g=(10\bar{1}1)$, $\lambda=1.40\text{\AA}$) shows dark dots corresponding to the positions of superscrew dislocations and their associated micropipes. They are the origins of swirling networks of basal plane dislocations, D. The dye impregnating the micropipes has made them much more prominent in the conventional optical micrograph in figure 3, where they appear as black lines. Figure 4 shows a fluorescence micrograph of the same area taken in the plane of focus at the wafer's surface. Micropipes, P, appear as bright specks against a dark matrix of SiC. The cross section of the emergent micropipes appear as circles or ellipses filled with fluorescence. The fluorescent columns of the micropipes that lie below the plane of focus appear as halos surrounding the bright specks. In the specimen examined here, no micropipes below $0.6\mu\text{m}$ in diameter were observed.

Figure 1.

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X-Ray Topography and Laser Scanning Confocal Microscopy of a Longitudinal Cut 6H-SiC Wafer *	X19C
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The defects characteristic of PVT 6H-SiC single crystals are super screw dislocations, which run roughly parallel to the c-axis and the crystal growth direction, and a network of regular dislocations which lie in and have Burgers vectors parallel to the basal plane. Super screw dislocations with very large Burgers vectors are often associated with optically visible hollow cores or "micropipes." Figures 1 to 4 show views of a micropipe in a portion of a wafer cut along the $(10\bar{1}0)$ plane. Figure 1 is an optical micrograph, showing that the dye-filled micropipe runs the length of the sample. In figure 2 an LSCM image of this micropipe, appears white on a black background. The diameter of the micropipe varies from 0.8 to $1.4\mu\text{m}$ along its length. The SWBXT image ($g=(0006)$, $\lambda=0.65\text{\AA}$) in figure 3 is sensitive only to displacement components lying in the axial direction. Figure 4 is a SWBXT image of a reflection ($g=(11\bar{2}0)$, $\lambda=0.64\text{\AA}$) whose g vector lies in the basal plane, sensitive only to components of displacement which are parallel to this g . In this image, the contrast of the superscrew dislocation image arises largely from the surface strains on the micropipe cavity. Dislocations, D, with Burgers vectors lying in the basal plane are periodically emitted from the superscrew dislocations along the length of the micropipe. The strain contrast from the dislocations appears strongest at the points where the dislocations are emitted. Comparison of figure 2 with figure 4, shows that the micropipes periodically dilate and constrict along their lengths, and that the periodicity of these diameter fluctuations appears to be the same as that of the emission of basal plane dislocations.

Figure 1.

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SYNCHROTRON WHITE BEAM X-RAY TOPOGRAPHIC CHARACTERIZATION OF PVT 3C-SiC CRYSTALS *

X19C

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Synchrotron White Beam X-ray Topography (SWBXT) has been used to study (100) 3C-SiC single crystal grown by the sublimation PVT technique at Howard University. Figures 1(a) and (b) are transmission synchrotron topographs recorded from the same area of the 3C-SiC wafer. Figure 1(a) shows that the 3C-SiC wafer is a single crystal. Although there are many contrast features on the topograph, no individual dislocations or slip bands can be resolved. The overall poor quality of the image suggests that the crystal may contain a high density of defects. The most striking features in figure 1(a) are the white patches, indicated by arrowheads. These white patches correspond to square shaped defects observable by optical micrograph with polarized light. Each square defect actually consists of four planar defects forming a pyramid, and as such are referred to as "pyramidal defects". In fact, the four planar defects in each pyramidal defect were found to be parallel to the four {111} planes with their four sides parallel to the [110] crystallographic directions. In figure 1(b) the "pyramidal defects" were imaged exclusively as dark patches. The correlation of the dark patches with the "pyramidal defects" is clearly demonstrated. Detailed analysis suggest that the "pyramidal defects" may be associated with extended planar faults parallel to the {111} planes. These faults are decorated with impurities or impurity clusters (the inclusions) and therefore there are large strains associated with them. Further investigation is needed to elucidate the nature of these pyramidal defects.

Figure 1. Transmission synchrotron topographs recorded from (100) 3C-SiC wafer.

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Microemulsion-Oil Interfaces in Ternary Liquid Systems

X19C

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X-ray reflectivity and surface diffuse scattering were used to study the microemulsion-oil (liquid-liquid) interface in a ternary system of water, decane, and C_4E_1 ($CH_3(CH_2)_3(OCH_2CH_2)OH$). These systems exhibit ultra low surface tensions and are expected to have large amplitude thermal fluctuations at the interfaces (similar to those at the oil-monolayer-water interface recently discussed by McClain et al. in Phys. Rev. Lett. 72, 246 (1994)).

Preliminary data taken at the X19C liquid surface scattering spectrometer is shown below for scattering from the oil-microemulsion interface of a C_4E_1 -water-decane (1:1:3 by volume) mixture at $35.00^\circ C$. The solution is in a vapor-tight polycarbonate sample cell. X-rays pass through 0.001" mylar windows attached to the body of the cell and through the upper oil phase to scatter off the interface.

Specular reflectivity data measured as a function of the wave vector normal to the interface are shown in Fig. 1. Surface diffuse scattering measurements as a function of the exit angle beta (in the plane of incidence) for a fixed incident angle of 0.055 degrees are shown in Fig. 2. Preliminary analysis of the specular reflectivity data and the surface diffuse scattering data indicates an interfacial roughness of $51 \text{ \AA}$ $\pm 3 \text{ \AA}$. This roughness can be attributed to surface-tension dominated thermal fluctuations at the interface.

Figure 1. Reflectivity data as a function of wave vector normal to the interface.

Figure 2. Surface scattering showing peaks at the critical angle for total reflection and at the angle for specular reflection.

X-ray Scattering Studies of the Passive Film on Fe(110)

X20A

Alison J. Davenport, Carissima M. Vitus (DAS, BNL), and Michael F. Toney (IBM Almaden Research Center)

Despite decades of work, there is still little understanding of the passivating oxide films that protect (normally reactive) metals from corrosion. This is because they are very thin (typically a few nanometers) and are formed in an aqueous environment so that ex situ measurements are susceptible to any changes in the film when they are removed from the solution in which they grew. The structure of the passive film on iron has been the subject of particularly intense study (Refs. 1 and 2, and references therein), but there is still little consensus on questions as basic as to whether the film is amorphous or crystalline. However, recent in situ STM images of passive films on iron (2) suggest that the surfaces are crystalline with proposed structures ($\gamma\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$) that are supported by in situ XANES and EXAFS measurements (1). To confirm and expand these recent findings, we have performed in-situ and ex-situ X-ray scattering experiments on the passive oxide formed on Fe(110) single crystals. Such measurements probe the entire film rather than just the surface layer.

The Fe(110) single crystal was passivated by potentiostatic polarization for ≈ 60 minutes at +0.4V vs MSE in borate buffer (pH 8.4). In situ data were obtained with the electrode poised at this potential, while for our ex-situ measurements, the electrode was emersed and placed in a flowing He atmosphere. Our methodology was to perform detailed measurements ex situ, where the background X-ray scattering is small (since there is no electrolyte), and then collect selected in situ data to compare with the ex situ measurements. In such a comparison, there was excellent agreement between the in situ and ex situ data, showing that the passive film formed under our conditions was not altered by removal from the electrolyte and from potential control.

The observed diffraction pattern from the passive oxide on Fe(110) is that of $\gamma\text{Fe}_2\text{O}_3$ or Fe_3O_4 , which confirms the STM and XANES results. At this point we cannot distinguish between these two structures, although a careful intensity analysis should permit this distinction. Our data also show that perpendicular to the surface $\gamma\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4(111) \parallel \text{Fe}(110)$, while parallel to the surface $\gamma\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4(\bar{1}10) \parallel \text{Fe}(002)$. The latter orientational relationship is quite reasonable, since in these directions the lattice mismatch between the metal and oxide is less than 0.4%. From the diffraction peak widths, we find that parallel to the substrate the grain size is $\approx 4\text{-}5\text{nm}$, and that there appear to be planar defects, such as stacking faults. The data also show that the passive oxide is twined (e.g., both $\gamma\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4(111)$ and $\gamma\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4(\bar{1}\bar{1}\bar{1})$ orientations are observed), although there is an asymmetry to this twinning that we do not presently understand.

- [1] A.J. Davenport and M. Sansone, J. Electrochem. Soc. 142, 725-730 (1995).
- [2] M.P. Ryan, R.C. Newman, and G.E. Thompson, J. Electrochem. Soc. 142, L177 (1995).

GIXD Measurements of Initial Strain Relaxation in $\text{Si}_{1-x}\text{Ge}_x$ Thin Films

X20A

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Strain-relaxed step-graded SiGe layers have been shown to have relatively low threading dislocation densities and thus can serve as substrates for high-mobility FETs having strained Si, SiGe, or Ge channels. Step-graded structures grown by UHV-CVD at low temperature relax *via* a Modified Frank-Read

(MFR) mechanism by which dislocations are formed by the reproduction of "corner dislocations" that glide into the substrate on {111} planes. A series of experiments have been performed at X20A using triple-axis x-ray diffraction to study the properties of strain relaxation in these structures. (For references, please see X20 publications list). We also have used grazing-incidence x-ray diffraction (GIXD) to measure the initial stages of strain relaxation in thin single-composition SiGe films epitaxially grown on Si(100).

GIXD permits the direct measurement of in-plane lattice parameters of SiGe films that are too thin to yield good results from normal-geometry triple-axis techniques. We see a unique "X"-shaped pattern in H-K reciprocal space maps of diffracted x-ray intensity from SiGe films that have relaxed via the MFR mechanism.

Contours of intensity are seen along the $\langle 110 \rangle$ directions from the $(-4\ 0\ 0)$ reciprocal lattice peak with the introduction of the first dislocations. For higher dislocation densities the "X"-shaped contours are anisotropically distorted; and a satellite peak, corresponding to the lattice parameter for a partially relaxed film, becomes identifiable at lower H.

In contrast, H-K reciprocal space contours from thin SiGe films that have relaxed by roughening and subsequent random nucleation of dislocations display broad, oval-shaped contours centered at the $(-4\ 0\ 0)$ reciprocal lattice point for the film.

Numeric simulations of GIXD from a variety of dislocation arrangements were performed in order to understand the origin of the "X" pattern. We show that this pattern arises from an array of long misfit dislocations running in the $\langle 110 \rangle$ directions. We also calculate accurate values for the composition and strain in these SiGe layers from the measured in-plane and out-of-plane lattice parameters.

(Submitted to Journal of Applied Physics).

Figure 1. H-K reciprocal space contours of 700 Å of $\text{Si}_{0.75}\text{Ge}_{0.25}$ grown at 500°C and relaxed 4% by the MFR mechanism.

Interfacial Roughness and Giant Magnetoresistance in Sputtered Co/Rh Multilayers as Studied with X-ray Scattering

X20A

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Recently, there has been a great deal of interest, from both a fundamental and applications standpoint, in magnetic thin films and multilayers, since these materials can exhibit magnetic properties that are spectacularly different from those found in bulk materials. For instance, multilayers of ferromagnetic and nonmagnetic materials show a giant magnetoresistance (GMR), or change in resistance upon application of a magnetic field. While it is generally accepted that the scattering of conduction electrons at the interface plays an important role in GMR, it is not clear how interfacial roughness affects this scattering and the GMR.

We have conducted specular and diffuse X-ray reflectivity studies of epitaxial Co/Rh (110) and (100) multilayers with the aim of addressing this relationship. The Co/Rh(110) multilayers exhibit dramatically anisotropic GMR, approximately twice as large for current flow along the (001) direction as along (110). Likewise, diffuse reflectivity data (see Fig. 1) show that the interfacial roughness is anisotropic. Specifically, the correlation length of the roughness in the plane of the film is much shorter along the (001) direction than along (110), e.g., $\leq 100\text{\AA}$ and $\approx 500\text{\AA}$, respectively. In contrast for Co/Rh(100), the roughness and GMR are both isotropic. These data suggest that the difference in GMR is due to the difference in roughness correlation length, with higher GMR resulting from a shorter correlation length.

Figure 1. Diffuse scattering data at the fourth multilayer Bragg peak for Co/Rh(110). These have been corrected for sample area and X-ray absorption, but not dynamical effects. $Q_{\parallel}$ is the component of the scattering vector parallel to the surface. The lines show best fits to these data, which were used to determine the correlation lengths.

Structural Phase Transitions and Magneto-Elastic Effects in $\text{USb}_{0.8}\text{Te}_{0.2}$ and USb.

X20B

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At room temperature the uranium antimonides substitutionally doped with tellurium ($\text{USb}_{1-x}\text{Te}_x$) are paramagnetic with a rocksalt structure. Pure USb orders as a triple-q antiferromagnet (AF) for temperatures below the Néel temperature ($T_N \sim 203\text{K}$) [1]. Replacement of the antimony with tellurium increases the ferromagnetic interactions and this gives rise to a low temperature ferromagnetic phase in the compound $\text{USb}_{0.8}\text{Te}_{0.2}$ ($T_C \sim 175\text{K}$, $T_N \sim 205\text{K}$) [2]. Our previous studies at the NSLS have concentrated on the resonantly enhanced magnetic scattering from the AF phases of these materials.

It is not straightforward to investigate any ferromagnetic diffraction signal owing to its superposition on the far larger charge scattering from the lattice.

It has been reported from x-ray powder diffraction studies that $\text{USb}_{0.8}\text{Te}_{0.2}$ distorts rhombohedrally on entering the ferromagnetic (F) phase [3]. These structural distortions result from the [111] ordering direction of the magnetic moment. We intend to gain a greater understanding of the magnetic properties of these materials through a detailed study of the lattice behavior, particularly in the F-phase of $\text{USb}_{0.8}\text{Te}_{0.2}$. We have made 4-circle diffraction measurements using 17.4 keV radiation at the following reciprocal lattice points (as indexed in the high temperature cubic phases): (0, 0, 8), (0, 0, 10), (10, 0, 10) and (8, 8, 8). In figure 1 we illustrate the longitudinal splitting of the (10, 0, 10) peak in $\text{USb}_{0.8}\text{Te}_{0.2}$ on passing through T_C . From this splitting we extract a rhombohedral bond angle at saturation of $\alpha = 89.853^\circ \pm 0.015^\circ$. This agrees well with the result $\alpha = 89.854^\circ \pm 0.010^\circ$ which may be inferred from the work of Hulliger and Vogt [3].

In figure 2 we illustrate an interpolated map of the observed scattering from (8, 8, 8) at 168K projected down onto the $K=0$ plane. The measurements obtained from USb show far less dramatic behaviour owing to the lack of any ferromagnetic ordering. A paper describing in detail our observations from $\text{USb}_{0.8}\text{Te}_{0.2}$ is in the final stages of preparation.

[1] S.C. Perry, et al. (To be published); [2] W.J. Nuttall, et al. Phys. Rev. B 52, 4409, (1995); [3] F. Hulliger and O. Vogt, Physica B 102, 316, (1980).

Figure 1.

Figure 2.

In-situ, Simultaneous Three-Probe Measurement of Structural Transformations in Metal Silicides.

X20C

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The formation of low-resistance-silicide source, gate, and drain contacts for sub-micron circuits is a critical processing step in semiconductor CMOS logic and memory manufacturing. Instrumentation has been developed for the *in-situ* monitoring of structural transformations to low-resistance phases in these materials, in the form of blanket thin films, arrays of patterned lines (gratings), and microelectronic structures.

A special furnace chamber has been constructed which performs rapid thermal annealing (RTA) ramps up to 35 °C/sec, and has the capability for simultaneous real-time measurement of x-ray diffraction, four-probe sample resistivity, and optical scattering. At a bending magnet beamline equipped with synthetic multilayer monochromator optics and a linear diode array detector which intercepts $\sim 10^\circ$ in 2θ , changes can be measured on a millisecond timescale. Not only can fast processes be monitored in this way, but a large matrix of materials sets and process parameters can be quickly evaluated. The average cycle-time for a phase transformation measurement and sample change with this configuration is ≤ 20 minutes.

Results have been published of measurements of TiSi_2 C49 (high resistivity) to C54 (low resistivity) transformations in arrays of sub-micron lines [1] and CMOS gate conductors [2]; identification of a metal-rich Ti silicide [3]; and the effect of a Ti interlayer on CoSi_2 phase formation [4].

1. R.A. Roy, et al., Appl. Phys. Lett. 66(14), 1732 (1995).
2. L.A. Clevenger, et al., J. Mater. Res. 10(9), 2355 (1995).
3. L.A. Clevenger, et al., Thin Solid Films, submitted.
4. C. Cabral, Jr., et al., Mat. Res. Soc. Symp. Proc. 375, 253 (1995).

Effects of Rubbing Parameters on Surface Orientation of BPDA-PDA Polyimide

X20C

James M. Sands and Sanat K. Kumar (The Pennsylvania State University), Thomas P. Russell and Michael F. Toney (IBM Almaden Research Center)

We previously showed that rubbing BPDA-PDA polyimide films orients most of the polymer chains within a thin surface region along the rubbing direction [1] and that this results in the alignment of liquid crystals in contact with the polyimide. In an effort to understand the mechanism of polyimide surface orientation and liquid crystal alignment, grazing incidence X-ray scattering (GIXS) has been applied to characterize the effects of various rubbing parameters on the resulting polymer orientation. In these experiments, BPDA-PDA thin films rubbed under varying load, distance, and rate were examined. By looking at the X-ray scattering with the scattering vector aligned parallel and perpendicular to the direction of the rubbing, one can establish the degree of orientation in the polymer surface with a depth resolution of 50Å. GIXS profiles show that there is a critical load and distance required in order to cause surface orientation (Figure 1a). Using the onset of discernible orientation as a gauge, the force required to cause orientation of the polyimide molecules is found to be quite small (Figure 1b). The small force is surprising as one expects significant restrictions to chain mobility, due to the high T_g of the bulk polymer (653 K). The ease with which the polymer surface orients questions the relationship of T_g (a bulk phenomenon) to thin films.

[1] M.F. Toney, et. al., Nature, 374, 709 (1995).

Figure 1. a) GIXS profile for 573K imidized BPDA-PDA buffed under $2\text{gm}/\text{cm}^2$ at $1\text{cm}/\text{s}$. Solid line is Q oriented parallel to rubbing direction. Dashed line is Q oriented perpendicular to the rubbing direction. Insets show the distance over which the samples were buffed. b) GIXS scans showing the degree of orientation in the surface under various loading. Data is obtained by fixing incidence angle and scattering position and rotating the sample in the beam ($Q = 0.81\text{\AA}^{-1}$). Distance of buffing is 50cm. Direction of rub is 0. Inset shows buffing loads.

Synchrotron X-ray scattering study of the N-IC phase transition in Rb_2ZnCl_4	X17B1, X20C
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Below $T_c \approx 303$ K, Rb_2ZnCl_4 undergoes a continuous phase transition from a normal crystalline (N) phase, to one-dimensionally modulated incommensurate (IC) phase characterized by a modulation wavevector q . The transition can be characterized by a two-component primary order parameter corresponding to the amplitude and phase of the modulation wave, the transition is expected to belong to the 3D-XY universality class. Higher harmonics of the modulation wave form a class of secondary order parameters for the transition.

Measurements of the temperature dependences of the intensities of the satellite peaks corresponding to the primary order parameter and the next two higher harmonics were performed on X20C. The resulting order parameter exponents are $\beta_1 = 0.35 \pm 0.01$, $\beta_2 = 0.87 \pm 0.01$, and $\beta_3 = 1.50 \pm 0.04$, in good agreement with recent theoretical predictions for the 3D-XY universality class.

Figures 1 and 2 show the critical scattering above T_c measured on X20C and X17B1 respectively. The second, sharp, component in the X20 data corresponds to critical fluctuations on length scale ~ 10 times those of the broad component visible in both data sets. The penetration depth of the 10 keV X-rays used on the X20 experiment was $\approx 20 \mu\text{m}$, whereas the 60 keV X17B1 experiment was performed in transmission, the ≈ 2 mm penetration depth being approximately equal to the sample thickness. This data is evidence for a near-surface origin of the second length scale scattering. The measured temperature dependence of the width of the broad component of the critical scattering results in a value of the inverse correlation length exponent $\nu = 0.66 \pm 0.02$, in agreement with the 3D-XY result.

Figure 1. Critical scattering measured on X20C. Note the presence of a second component in the scattering.

Figure 2. Critical scattering measured on X17.

Inelastic X-Ray Scattering Study of Diamond *	X21
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W.A.Caliebe, C.-C.Kao, J.B.Hastings (NSLS), M.H.Krisch, F.Sette (ESRF, France), K.Hämäläinen (University of Helsinki, Finland)

We have measured the dynamical structure factor $S(Q, \omega)$ of diamond with an energy resolution of 1 eV FWHM and Q between $0.7 \text{ \AA}^{-1}$ and $3.4 \text{ \AA}^{-1}$ in the highly symmetric (001) and (111) direction. In this range the spectra are dominated by bandstructure effects, which results in completely different shape and behavior of the spectra in both directions.

The spectra in the ΓL direction are dominated by transitions from a low lying valence band into almost parallel conduction bands. The resulting peaks show almost no dispersion but they change in intensity with increasing Q . This change results from the q -dependence of the transition matrix elements. The ΓX direction shows less and broader peaks. The broadening can be explained by a larger bandwidth of each band.

Figure 1. Spectra of diamond in the ΓX direction

Figure 2. Spectra of diamond in the ΓL direction

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W.A.Caliebe, C.-C.Kao, J.B.Hastings (NSLS), M.H.Krisch, F.Sette (ESRF, France), K.Hämäläinen (University of Helsinki, Finland)

Inelastic X-Ray Scattering is a useful technique to study electronic excitations in solids and liquids. By tuning the energy difference between the monochromator and the analyzer to an absorption edge, this edge can be studied with a much higher incident energy. By changing the scattering angle, different absorption channels are excited which results in a change of the line shape.

We studied with high energy resolution the Li K-edge at ~ 60 eV with an incident energy of 7.9 keV for different scattering angles. The spectra are shown in figure 1. For small Q , they show a relatively narrow peak at an energy loss of 62.5 eV. This peak increases with increasing Q up to $Q=5.7 \text{ \AA}^{-1}$. At medium Q , this peak broadens and shifts finally at higher Q to 61.5 eV. The increase in intensity can be explained by the expression given by Mizuno and Ohmura[1]. The shift can be explained by the fact that we deal with two peaks, which overlap at medium Q and cause the broadening. The peak at 62.5 eV can be attributed to the $1s \rightarrow 2p$ transition while the peak at 61.5 eV is the $1s \rightarrow 2s$ transition which is optically forbidden. For this reason we do not see this transition at small Q but at higher Q the matrix element belonging to this transition increases and finally dominates the whole absorption process. A more detailed quantitative analysis is in progress.

[1] Yikio Mizuno and Yoshihiro Ohmura, J. Phys. Soc. Jap. 22, 445, 1967

Figure 1. Inelastic X-Ray Scattering spectra for different Q . The vertical lines indicate the two peak positions corresponding to the $1s \rightarrow 2p$ (62.5 eV) and $1s \rightarrow 2s$ (61.5 eV) transition.

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The oxidation/reduction chemistry of nickel is of key importance in fields ranging from battery technology to organometallic catalysts. Features in the Ni K and L edge x-ray absorption spectra and K- β fluorescence spectra of model complexes been shown to be sensitive to the metal's effective charge, but each of these techniques suffers from some disadvantage as a diagnostic tool for unambiguously assigning charge state to an unknown sample. We have explored the possibility of using the K- γ fluorescence as an improved probe. We are also able to compare our results with the predictions made with the current theoretical model for Ni line shapes.

High resolution fluorescence measurements were carried out on beamline X-21 on three samples (the salts of Ni(II)tetramethylcyclam, Ni(I) tetramethylcyclam, and Ni(II) tris-bipyridine) representing nickel in the +2 low-spin, +1, and +2 high-spin states. The samples were excited below, on, and above the K-edge resonance. As shown in the figure below, the main peak of the K- γ fluorescence is shifted by approximately 2 eV when a sample is reduced from Ni(II) to Ni(I) (note elastic scatter at excitation energy of 8340 eV). This is of the order of the FWHM of the line, and hence a mixture of the two oxidation states would be easily resolved as a broad, double peaked feature.

Figure 1. High resolution fluorescence spectra of Ni^{+1} and Ni^{+2} for an incident energy of 8340 eV. An energy shift of ~ 2 eV of the fluorescence line is clearly visible in the spectra and can be attributed to the different oxidation state.

* Supported by US DOE under contract # DE-AC02-76CH00016.

High resolution Compton scattering from Li

X21

K. Hämäläinen, S. Manninen (Helsinki U., Finland), C.-C. Kao, W. Caliebe, J. B. Hastings (BNL), A. Bansil (Northeastern U.)

Compton scattering is traditionally used to measure the momentum densities in solids. However, the moderate energy and momentum resolution have prevented to look for finer details in the measured spectra. At X21, momentum resolution of 0.02 a.u. at 8 keV incident photon energy is achieved by high resolution backscattering spectrometer based on a spherically bent Si(111) analyzer crystal. Being by factor of five better than ever achieved before this has opened up new possibilities to use Compton scattering as a tool to study Fermi surface related issues.

We have concentrated on two things. First, to look for Fermi surface footprints in the measured Compton profile via umklapp processes. When the directional Compton profiles are measured from single crystal samples by placing the scattering vector along different crystal directions the 3-dimensional Fermi surface can be mapped. Secondly, we have measured the Fermi break with high resolution and statistical accuracy. In this case the high resolution Compton scattering is a unique direct probe to study the electron-electron correlation effects at the Fermi surface.

The preliminary results suggest the nonexistence of the expected sharp features in the measured Compton profiles. Furthermore, the Fermi surface seem to be smeared much more than would be expected by the theoretical calculation even with electron-electron correlation included. The theoretical work to explain the observations are in progress.

Figure 1. Left: Total Compton profile of Li measured by scanning the incident energy. Right: Fermi break of Li ($q||$ [110]). The solid line represents the KKR theory.

Inelastic x-ray scattering studies of electronic excitations

X21

J.P. Hill, C.C. Kao, W.A. Caliebe, D. Gibbs (BNL), D. Reznik (NIST) and J.P. Wilcoxon (SNL)

Traditionally the study of electronic excitations has been performed with techniques such as electron scattering and photoemission. Inelastic x-ray scattering offers a new window on the study of such processes. It has the advantage that the scattering is weak, i.e. in the kinematic limit, for all momentum transfers so that both collective and single-particle excitations may be studied and the results simply interpreted. In this work, the spectrometer was configured to provide a 1 eV resolution with the ability to scan both the incident and final energies. This is particularly flexible arrangement, allowing a wide range of electronic phenomena to be studied.

We have carried out preliminary experiments on a number of electronically interesting materials. These include metallic clusters and in particular, mono-dispersed samples of aluminum. Here the interest lies in quantum finite size effects which are expected to change the excitation spectrum for small ($\approx 30 \text{ \AA}$) cluster size. Initial experiments on large clusters (500 $\text{\AA}$) exhibit bulk-like behavior and work is currently in progress on smaller cluster sizes. We have also studied carbon nanotubes. These consist of graphite sheets "rolled up" to form tubes on the order of 10 $\text{\AA}$ in diameter and 1 μm long. For thin walled cylinders, a surface plasmon at 15 eV was seen in electron diffraction experiments. In our x-ray work, we did not observe the surface plasmon, however a peak due to the interband transitions is observed at 5 eV. In addition a peak at 30 eV, which is ascribed to a plasmon excitation of all four valence electrons is observed. In fig. 1, we show the dispersion of these features. Finally, the technique of resonant inelastic x-ray scattering, in which the incident photon energy is tuned to an absorption edge has been explored in the vicinity of the L_{III} edge of holmium. Data analysis is ongoing.

Figure 1. Energy loss spectra from carbon nanotubes, taken at a number of momentum transfers.

E. D. Isaacs (AT&T Bell Labs), C. A. Burns, (Western Michigan University), T. Thio, J. W. Bennett (NEC Research Institute), W. Caliebe, and C.-C. Kao (BNL)

Mott-Hubbard systems are interesting because they display a rich variety of ground states not predicted by simple band theory. In particular, metal insulator transitions can occur as a result of electron correlations.

In $\text{NiS}_{2-x}\text{Se}_x$ there is a Mott-Hubbard metal-insulator transition for $x \sim 0.5$ at a temperature of ~ 80 K. The $\text{NiS}_{2-x}\text{Se}_x$ is an excellent system in which to study this transition since there is no change in the symmetry of the system as a result of the transition, as is seen in most other Mott-Hubbard insulators. Recent photoemission data [1] has suggested that the addition of Se to NiS_2 crystals reduces the size of the insulating gap, inducing the transition to the metallic phase at lower temperatures.

Our data was taken on a single crystal of $\text{NiS}_{1.5}\text{Se}_{0.5}$ which was placed in a closed cycle refrigerator with a Be window to allow x-ray access. Measurements were taken at incident energies of 8344 eV in order to take advantages of resonant scattering from the Ni. The scattered intensity was measured as a function of energy loss for energy losses from -5 to 25 eV with a resolution of ~ 1 eV. We observed a peak in the spectrum at an energy loss of about 4.5 eV. We believe that this feature is due to the Mott-Hubbard gap in the crystal. Even with the resonant enhancement we only had about 1/2 count per second in the loss peak. Data was taken at several different reciprocal lattice vectors in both the insulating and metallic phases.

Our measurements did not show any significant changes between the metal (T ~ 100 K) and the insulator (T=70 K) phases. Such effects have been seen in the Mott-Hubbard insulator V_2O_3 [2]. Photoemission studies on $\text{NiS}_{2-x}\text{Se}_x$ show a shift of about 0.15 eV for the valence band (at low q). We did see q-dependent changes in the energy loss peak. The change in intensity is due in part to a spectral weight shift to the Compton energy ($\hbar^2 q^2 / 2m$), but there is also evidence for dispersion of the peak. Future studies of this system with higher energy resolution are planned.

[1] A.Y. Matsuura, Z.-X. Shen, D. S. Desseau, C.-H. Park, T. Thio, J. W. Bennett, and O. Jensen, preprint of article submitted to PRL.

[2] E. D. Isaacs, P. M. Platzman, P. Metcalf, and J. M. Honig, submitted to PRL.

Figure 1. Mott-Hubbard Gap in $\text{NiS}_{1.5}\text{Se}_{0.5}$ in the metallic phase at 100 K at several momentum transfers. Numbers in parentheses are Compton Energies.

N. Jisrawi, G. Reisfeld (BNL-Physics), H. Wiesmann (BNL-DAS), T. Thurston, M. W. Ruckman, B. Ocko and M. Strongin (BNL-Physics)

Materials changes during the electrical discharging of a thin film Ni-MH battery were investigated using x-ray diffraction. The metal-hydrogen anodes were Nb/Pd multilayers of the configuration Nb/Pd/Nb/Pd where the Nb thickness ranged from 200 to 800 Å and the Pd thickness was 200 Å. The multilayers were deposited on Cr-coated glass and placed in a thin windowed electro-chemical cell containing a 1M KOH electrolyte. A two terminal configuration employing a NiOOH counter electrode was used. After charging the cell to a two terminal voltage of 1.2 V, the cell was discharged through a 10 KΩ resistor and the current monitored. The rate of discharge was slow and x-ray diffraction spectra taken at the points indicated on the figure 1. The x-ray spectra in figure 2 show the amount of hydrogen in the Nb or Pd because their lattices expand when hydrogen is introduced into the lattice.

The Nb[110] and Pd[111] Bragg peaks shift to smaller 2θ when charged with hydrogen and return to the metallic position when discharged. It is believed these spectra are among the first taken during the operation of a battery and show how the hydrogen content is related to battery function. The limited amount of electrolyte over the electrode affects the reaction at the electrode surface and may account for the anomalous drop in the battery current before all of the hydrogen is discharged from the anode.

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Figure 1. Battery discharge curve (i vs V).

Figure 2. X-ray spectra taken at the positions marked on figure 1.

X-ray identification of peaks in cyclic voltammetry from Nb/Pd multilayers in a KOH electrolyte *

X22A

N. Jisrawi, G. Reisfeld (BNL-Physics), H. Wiesmann (BNL-DAS), T. Thurston, M. W. Ruckman, B. Ocko and M. Strongin (BNL-Physics)

We conducted a x-ray diffraction study of hydrogen uptake by glass-supported Nb/Pd multilayers in an electrochemical experiment.

The metal-hydrogen anodes were Nb/Pd multilayers of the configuration Nb/Pd/Nb/Pd where the Nb thickness ranged from 200 to 800 Å and the Pd thickness was 200 Å. The multilayers were deposited on Cr-coated glass and placed in a thin windowed electro-chemical cell containing a 1M KOH electrolyte. A two terminal configuration employing a NiOOH counter electrode was used.

The samples were charged and discharged by a standard cyclic voltammetry apparatus over a voltage range of -1.4-0 V at a scan rate of 1 mV/s. The rate of scanning was slow and x-ray diffraction spectra taken at the points indicated on the figure 1. The x-ray spectra in figure 2 show changes in the amount of hydrogen in the Nb or Pd because their lattices expand when hydrogen is introduced into the lattice. The Nb[110] and Pd[111] Bragg peaks shift to smaller 2θ when charged with hydrogen and return to the metallic position when discharged. It is believed these spectra represent one of the first in-situ probes of hydrogen charging of an electrode using synchrotron radiation-based x-ray diffraction and provide a convincing identification of CV peaks with the hydrogen phases formed during electrolytic charging of a thin film bimetallic electrode.

Figure 1. Cyclic-voltammetry (CV) for a Nb/Pd multilayer.

* This work was supported by the US-DOE Div. of Materials Science under CRADA BNL 94-03 and Contract No. DE-AC02-76CH00016.

Figure 2. X-ray spectra taken at the positions marked on figure 1.

Microstructural Study of at-C Films: Relation to Residual Stresses *

X22A

L. J. Martínez-Miranda (U. of Maryland), J. P. Sullivan, T. A. Friedmann, M. P. Siegal (SNL), T. W. Mercer, N. J. DiNardo (Drexel U.)

Amorphous tetrahedrally coordinated carbon films (at-C) have potential in a variety of applications. It is important to understand their structural, mechanical and electrical properties and how these relate to the method of film processing. These films consist of a mixture of carbon - carbon sp^2 - sp^3 bonds, grown in the absence of hydrogen.

We have combined reflectivity and small angle scattering measurements to obtain structural information on at-C films prepared by pulsed laser deposition in a high vacuum environment, at different laser energies. The experiments were performed using 10.3keV x-rays. Experimental resolution of $\Delta E/E = 10^{-4}$ was achieved by using a 5-bounce Si(111) monochromator and a 3-bounce Si(111) analyzer.

We have used the results of the reflectivity measurements to obtain information on the density of the films, as well as the presence of layering. The results of the small angle scattering measurements give information on any density contrast due to the distribution of sp^2 to sp^3 bonds within the films.

The density of the films varies between $2.8g/cm^3$ and $3.3g/cm^3$ as the laser energy density increases from $11J/cm^2$ to $44J/cm^2$, indicating an increase in the ratio of sp^3 to sp^2 bonded carbon in the films. This result correlates well with the films' stress and electrical resistivity measurements. The maximum film density decreases with increasing film thickness. In addition, the small angle scattering signal suggests the presence of regions in the films with a basic length scale of 10 nm. The small angle signal may arise as a result of internal layering within the film or as a result of a lateral density variation within the films. The latter may produce conductive paths within the films and may be responsible for the observed variations in the films' resistivity. At present we are performing a quantitative analysis of these results to ascertain the nature of this small angle signal.

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The commensurate-incommensurate transition of Br on the Au(100) electrode. X22A

B.M. Ocko, O.M. Magnussen (BNL/Physics), J.X. Wang (BNL/DAS), T. Wandlowski (Ulm)

Electrodeposited bromide on the Au(100) surface forms a commensurate $c(\sqrt{2} \times 2\sqrt{2})R45^\circ$ monolayer with a coverage of $1/2$ over a range of applied potentials. Here the bromide atoms reside in two-fold sites rather than four-fold hollows ordinarily found for this coverage. At a critical potential the bromide adlayer undergoes a continuous transition to a uniaxial-incommensurate $c(\sqrt{2} \times p)R45^\circ$ monolayer where p decreases from 1.00 to 0.87 in terms of the commensurate length. The incommensurate phase is well described a uniform compression and is inconsistent with sharp domain-walls. The quadratic scaling of the peak widths with the incommensurate component of the wavevector suggests that the incommensurate phase exhibits "cumulative disorder". The potential dependent structure of the bromide adlayer is in excellent agreement with the electrochemical characteristics.

Figure 1. Real space sketch (a,b) of the commensurate $c(\sqrt{2} \times 2\sqrt{2})R45^\circ$ and incommensurate $c(\sqrt{2} \times p)R45^\circ$ phase and the corresponding reciprocal space patterns (c,d).

Small Angle X-ray Scattering (SAXS) Investigations of Metal and Semiconductor Nanoscale Size Clusters X22A, X27A

T.R. Thurston (BNL), J.P. Wilcoxon, and S. Craft (SNL)

Recently, there has been a dramatic rise in interest in nanoscale size materials. This has occurred largely because new techniques have been developed to manufacture these materials in greater quantities. It has also been recognized that nanoscale size materials often have unique and desirable properties that are different from the corresponding bulk properties. For example, the catalytic properties can become greatly enhanced when a material is reduced to nanoscale dimensions.

Two of the most basic properties that must be characterized when making nanoscale clusters are the average cluster size and the polydispersity of the clusters in a sample. The size can often be roughly estimated from electron microscopy measurements, but the only way to determine both parameters while averaging over the entire sample volume is through small angle x-ray scattering experiments.

To fulfill this characterization need, we have constructed a Bonse-Hart camera which can be mounted at the X22A beam line. Unfortunately, the upstream monochromator crystal of this beam line scatters in a horizontal geometry, so we have had to place a vertically scattering collimator crystal before the sample position. This has usually been a 5-bounce channel cut Si(111) crystal. The analyzer crystal is also a 5-bounce channel cut Si(111) crystal. With this rather simple set up, we have been able to obtain a dynamic range of nearly 10^9 with a range in q from 10^{-4} to $10^0 \text{ \AA}^{-1}$.

The samples we have examined were made using an inverse micelle technique which produces samples with very good polydispersity characteristics. Therefore, the small angle scattering curves show interference effects (wiggles) and it is rather simple to then fit the SAXS data to obtain the size and polydispersity of a sample. We have examined a number of cluster samples including Au, Pd, Rh, and MoS_2 that have been prepared under differing conditions and with different average sizes. More materials will be examined in the future as the inverse micelle technique is developed further.

Figure 2. (a) Cyclic voltammogram from the Au(100) surface in 0.05 M NaBr and (b) the corresponding incommensurability (ϵ) as a function of the applied potential in both sweep directions $c(\sqrt{2} \times p)R45^\circ$ phase. The solid line is a power-law fit to the incommensurability with $\beta=0.40$.

Synchrotron X-ray Scattering Characterization of High Temperature Superconducting Wires	X27A, X22A
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T.R. Thurston, U. Wildgruber, N. Jisrawi, M. Suenaga, Y.L. Wang (BNL), and P. Haldar (IGC)

A CRADA between BNL and Intermagnetics General Corporation was begun in 1995 to use synchrotron x-ray scattering techniques for characterizing $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($T_c=110\text{K}$) 2223 superconducting wires. These wires show commercial promise; for example, higher magnetic field strengths in MRI machines will be attainable using this technology, provided the quality of the wires can be improved.

A major problem in characterizing the wires arises from the fact that the superconducting material is by necessity sheathed in silver cladding. We recognized that the intense x-ray flux available at a synchrotron source allows structural characterizations of these wires which are not possible with any other methods. We mention two of our major conclusions to date here.

We first discuss the differences between early wires made with a single filament of superconducting material compared to more recently made multifilament wires. Generally, the multifilament wires have shown better transport properties than the monofilament wires, but the reason(s) for this improvement have been nebulous. We have found, however, that the full width of the (200) peak of monofilament samples is systematically larger than the full-width of this peak in multifilament samples. Thus, the multifilament samples generally are better textured than the monofilament samples, which improves their transport properties.

In the second example, we consider the phase composition. The starting material for these tapes is 2212 $(\text{Bi,Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ ($T_c=85\text{K}$) phase, along with enough other materials to make 2223 after heat treatments. From analysis of two-theta scans, we have found varying amounts of 2212 in all samples studied to date, with the amount ranging from 4 to 40 percent in nominal 100 percent 2223 samples. Further, by rastering the sample through the x-ray beam, we have shown that the 2212 composition is not homogeneous along the length of all tapes. This data suggests that the phase development process must be examined more closely.

The effects of hydrogen adsorption/evolution and bisulfate coadsorption on the structure of underpotentially deposited Tl adlayers on Pt(111) *	X22A, X22B
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J.X. Wang, R.R. Adzic (BNL/DAS), B.M. Ocko, O.M. Magnussen (BNL/Physics)

Tl forms an incommensurate, aligned-hexagonal phase in acid and alkaline solutions at the most negative potentials prior to its bulk deposition or hydrogen evolution. The monolayer compresses, thus the Tl coverage increases, with decreasing potential. In acid solutions, this phase exists in the potential region where hydrogen adsorption and evolution occur in the absence of Tl^+ (Fig. 1). Underpotential deposition (UPD) of Tl suppresses hydrogen adsorption but does not shift the onset of hydrogen evolution. On the other hand, the competition of Tl UPD with hydrogen adsorption/evolution causes a slightly lowering of Tl coverage and a significant decrease of the in-plane ordering of the Tl monolayer.

In sulfuric acid solution, a $(\sqrt{3} \times \sqrt{3})R30^\circ$ diffraction pattern was observed over a 0.28 V wide potential range, which corresponds to the potentials between the two major peaks in the voltammogram. The involvement of both Tl and anion species in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice structure can be inferred from the absence of the diffraction signal in the solutions without either Tl^+ or bisulfates. Specular reflectivity data support the model with 1/3 monolayer of Tl at the hollow sites. It is, however, difficult to determine, directly from surface x-ray scattering, the bisulfate coverage and its adsorption sites. The similarity of bisulfate adsorption (without Tl) and coadsorption (with Tl) features in the voltammograms and the positive potential shift in the latter case suggest that bisulfate coadsorption is primarily through the interaction between bisulfate and Pt. This leads us to the model with bisulfates coadsorbing at the hollow sites of the Tl adlayer. In the top view picture shown in Fig. 1, Tl, Pt, S, and O are represented by the circles with the diameters corresponding to their relative atomic sizes. It can be seen that the model gives adequate interatomic spacings.

Figure 1. Tl coverages in the aligned-hexagonal (circles) and the $(\sqrt{3} \times \sqrt{3})R30^\circ$ (triangles) phases as a function of E and voltammograms in 0.05 M H_2SO_4 solutions with (solid line) and without (dashed line) 5mM Tl^+ . Sweep rate 20 mV/s.

* This work is supported by the DOE, contract DE-AC02-76CH00016

Structure of electrode surfaces in the course of electrocatalytic reactions: oxidation of CO, glucose and formaldehyde on reconstructed and unreconstructed Au(100) *

X22B

R.R. Adzic, J.X. Wang (BNL/DAS), B.M. Ocko, O.M. Magnussen (BNL/Physics)

Atomic scale information on the structure of a catalytic surface during the course of reaction has been a goal of surface scientists for many years. There is no information on the stability and activity of reconstructed surfaces in electrocatalytic reactions. Here we demonstrate the in situ application of the Surface X-ray Scattering (SXS) to electrocatalysis.

Grazing incident angle x-ray diffraction was used to determine the in-plane structure of the Au(100) surface during the oxidation of CO, glucose, and formaldehyde. The reconstruction of Au(100) gives rise to a diffraction peak around (1.205, 1.205, 0.1) position in reciprocal space. This peak is consistent with the hexagonal pattern with $\Delta = 1.205 \pm 0.002$, where Δ is the hexagonal wave vector along the (110) direction.

The electrochemical oxidation of glucose, formaldehyde and CO on gold single crystal electrodes are known as structure sensitive reactions with the reactant adsorption preceding the charge transfer. The adsorption of these molecules at negative potentials does not cause a lifting of the reconstruction of the Au(100) surface. The potential dependence of the intensity of the reconstruction peak at (1.205, 1.205, 0.1) was measured in HClO_4 and NaOH solutions in the absence and in the presence of the oxidation of organic molecules. The oxidation of these molecules occurs before, or at the onset of the lifting of the reconstruction. No significant change in the kinetics of the reconstruction lifting and recovering is caused by the adsorption and oxidation of glucose, CO and formaldehyde. The recovery of the reconstruction by the negatively charged electrode surface is a rather slow process. This slow recovery of the reconstruction allows us to measure the reaction rates at both reconstructed and unreconstructed surfaces over the same potential range.

Since the electrooxidation of the above three molecules are structure sensitive reactions, a distinct difference in the surface structure of the Au(100)-(1x1) and the reconstructed Au(100) is expected to produce an effect on their kinetics. The unreconstructed Au(100)-(1x1) surface was found to be more active than the hexagonally reconstructed Au(100) surface for all three reactions. The apparent heterogeneous rate constant is approximately one order of magnitude larger for the unreconstructed Au(100)-(1x1) surface. There are two possible origins of the observed difference in the activity of the reconstructed and unreconstructed Au(100) surfaces. First, the adsorption of these molecules is stronger on the open (100)-(1x1) surface compared to the hexagonal close packed surface. Besides that, the reaction is enhanced by the stronger adsorption of H_2O and AuOH which facilitate the oxidation of CO and chemisorbed intermediates in these reactions.

Surface freezing in binary mixtures of normal alcohols *

X22B

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Surface freezing has been observed recently at the free surface of pure alcohols, alkanes and binary mixtures of alkanes with different chain lengths. At temperatures up to 3°C above bulk freezing temperature, measurements reveal the formation of a crystalline monolayer on normal alkane mixtures and a bilayer on pure alcohols. X-ray reflectivity, grazing incidence diffraction and Bragg rod measurements have been carried out on the binary mixtures of the alcohol-alcohols and alcohol-alkanes. The measurements (Fig.1) show the formation of a bilayer on the alcohol mixtures. In some cases the upper layer of the frozen bilayer consisted only of the longer chain component and the lower layer of the shorter chain only. Grazing incidence diffraction indicates hexagonal packing and long range positional order within the surface layer. In order to describe the Bragg rod measurements (Fig.2) a lateral positional shift between the two layers is required as shown in the inset of Fig.2. This shift is similar to the shift observed for pure alcohols. A surface layer on alcohol-alkane mixtures was obtained only if the chain length of the alkane was about twice the length of the alcohol. In this case the transition from a monolayer to a bilayer has been observed. Additional phase transitions in the surface layer have been detected in surface tension measurements.

Figure 1. X-ray reflectivity for alcohol-alkane mixture $\text{C}_{22}\text{OH}(30\%)$ in C_{18}OH (circles). The solid line is a fit to the data. In the insert the e^- -density corresponding to the fit is plotted.

Figure 2. Bragg rod at in-plane diffraction peak position $q_r = 1.488 \text{ Å}^{-1}$ for 30% C_{22}OH in C_{18}OH . The solid line is a fit to the data, based on the real-space model in the inset.

* This work is supported by the DOE, contract DE-AC02-76CH00016

An X-ray Scattering Study of Methyl Eicosanoate *

X22B

W. J. Foster, M. C. Shih, P. S. Pershan (Harvard University)

Relaxed Langmuir monolayers of methyl eicosanoate were studied using Brewster angle microscopy (BAM) and grazing incidence x-ray diffraction (GIXD). The structure of the various phases in this system were determined and compared to previous isotherm and microscopy measurements.

At high pressure and low temperature, an untilted, orthorhombic phase, U(CS), is observed. As the temperature is increased, a second untilted, orthorhombic phase, U(S), is observed, beginning at $\sim 12^\circ\text{C}$. Above 21°C and at high pressure, a Rotator-IV-like phase is seen, with an undistorted, untilted structure.

At low pressure and low temperature, a crystalline phase with tilt toward nearest neighbor, $I(L_2'')$, is observed. At a temperature of $\sim 14^\circ\text{C}$, there is a transition to a phase with tilt toward next-nearest neighbor, $F(L_2')$, at low pressure. Finally, as the temperature continues to be raised at low pressure, there is a transition to a phase where the two $F(L_2')$ peaks have the same values of Q_{xy} , here called the τ phase.

Figure 1. π -T phase diagram of Methyl Eicosanoate. The phases are represented as follows: $I(L_2'')$, $\circ$ $F(L_2')$, $\times$ $U(CS)$, $\diamond$ $U(S)$, $\#$ $R(LS)$. The solid lines represent phase boundaries. In the case of the $U(CS)$ - $U(S)$ - $R(LS)$ transitions, the shaded regions represent observed limits of coexistence due to supercooling or superheating.

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X-ray Scattering Study of C_{60} -propylamine Adduct Monolayers at the Gas-Water Interface

X22B

M. Fukuto, P.S. Pershan (Harvard), D.Vaknin, and J.Y. Wang (Ames Lab and Iowa State)

In this project, we carry out specular reflectivity, small angle diffuse scattering and grazing incidence diffraction (GID) studies of Langmuir monolayers of nearly spherically symmetric fullerene derivatives. Although pure C_{60} does not form stable monolayers on water, Wang et al.[1] demonstrated that C_{60} -dodecylamine adduct[1] and C_{60} -propylamine adduct[2] do form homogeneous monolayers on water.

From the onset of the rise in surface pressure in the isotherm shown in Figure 1, one can conclude that the C_{60} -propylamine adduct molecules are essentially closely packed at about $A = 150 \text{ \AA}^2/\text{molecule}$, corresponding well with the expected cross sectional area for a single C_{60} -propylamine adduct molecule whose radius is slightly larger than that of the bare C_{60} (5.0 $\text{\AA}$). X-ray reflectivity measurements were performed on beamline X22B in July, 1995. The sample was held on a teflon trough in a sealed box under N_2 gas environment.

During the measurement reported here, the temperature and area/molecule were held at 18°C and $150 \text{ \AA}^2/\text{molecule}$, respectively. The reflectivity from the monolayer normalized to the Fresnel reflectivity of ideally flat water subphase, R/R_F , vs Q_z is shown in Figure 2. Our model of electron density profile along the surface normal is a step function whose two interfaces are distance d apart and are smeared out with a Gaussian roughness σ (inset). The fit based on this model of electron density and Born approximation is also shown in Figure 2. The fit gives a roughness σ of $3.1 \pm 0.2 \text{ \AA}$, and the film thickness d of $9.7 \pm 0.7 \text{ \AA}$, which is consistent with the diameter of one molecule, confirming that the film is one monolayer thick[2].

GID measurements on the same sample were hindered by excessive background scattering that was reduced considerably when the trough was filled with He gas instead of N_2 . The measurement will be repeated with high purity He gas.

Harvard contribution to this work was supported by NSF-DMR-94-00396. Ames Lab is operated by ISU for the DOE under Contract No. W-7405-Eng-82.

[1] J.Y. Wang et al., Thin Solid Films 242, 40 (1994).

[2] D. Vaknin et al., Langmuir 11, 1437 (1995).

Figure 1. Relaxation isotherm measured at $T = 17.5^\circ\text{C}$.

Figure 2. Reflectivity normalized by Fresnel reflectivity. The fit (solid line) corresponds to the electron density profile shown in the inset.

Influence of Quantum Impurities on the Soliton Lattice in CuGeO_3 . X22B

V. Kiryukhin, B. Keimer (Princeton University), J. P. Hill, A. Vigliante (BNL)

The interaction of localized impurities with correlated electron systems is a topic of great current interest in fields ranging from one-dimensional magnetism to high temperature superconductivity. A particularly interesting observation has recently been made in the spin-Peierls compound CuGeO_3 . In this material the spin chains consist of spin $1/2$ Cu^{2+} ions which interact antiferromagnetically with their nearest neighbors. In the absence of impurities the spin chains dimerize at low temperatures and form a nonmagnetic collective singlet state, the spin-Peierls state. Several groups have substituted dilute amounts of Zn^{2+} (spin-0) or Ni^{2+} (spin-1) for Cu^{2+} and found that the spin-Peierls state is rapidly replaced by a Néel state. This behavior undoubtedly reflects a competition between the interchain magnetic exchange interaction (which favors the Néel state) and the spin-lattice coupling (which favors the spin-Peierls state), but it has not yet been explained why the balance between these two interactions is tipped by diluting the spin-chains. The goal of our x-ray experiment was to elucidate the effects of impurities on the magnetic phase diagram of CuGeO_3 on a microscopic level. We studied the spin-Peierls superlattice reflections in two samples, $\text{Cu}_{0.985}\text{Zn}_{0.015}\text{GeO}_3$ and $\text{Cu}_{0.98}\text{Ni}_{0.02}\text{GeO}_3$, as a function of magnetic field and compared the results with analogous measurements in pure CuGeO_3 . Both samples undergo spin-Peierls transitions, but the transition temperature and the commensurate-incommensurate (C-IC) transition fields are depressed. While the C phase remains long range ordered, we found that the IC superlattice reflections are severely and anisotropically broadened (Fig. 1). In the spin chain direction the correlation length is the longest but even in this direction it is comparable to the average distance between the impurities. This presumably means that the magnetic solitons are strongly pinned at or near the impurities. While the IC wavevector discontinuously jumps to a nonzero value at the C-IC transition of pure CuGeO_3 signaling a (weakly) first order transition, there is no sign of such a discontinuity in the diluted samples. This indicates that the C-IC transition becomes second order as impurities are added, but further studies are necessary to prove this point definitively. We are also planning further experiments on samples with higher impurity concentrations in order to elucidate the crossover from the spin-Peierls to the Néel state.

Figure 1. Scans through the (3.5, 1, 2.5) reflection of $\text{Cu}_{0.985}\text{Zn}_{0.015}\text{GeO}_3$ a) parallel and b) perpendicular to the spin chains. The scan in b) is along (3.5, 1, 0), only 9° away from the a-axis. The temperature is 4K and the 10 Tesla and 11.6 Tesla data are below and above the C-IC transition respectively. The data for 11.6 Tesla were multiplied by 10.

Magnetic Phase Diagram of the Spin-Peierls System CuGeO_3 X22B

V. Kiryukhin, B. Keimer (Princeton University), J. P. Hill, A. Vigliante (BNL)

One Dimensional (1D) quantum magnetism has been the subject of great experimental and theoretical interest for the last three decades. In certain 1D magnets, coupling of the spin degrees of freedom to the lattice results in a low temperature structural transition, the spin-Peierls transition, at which the lattice dimerizes to lower the magnetic ground state energy. The lattice coupling allows the application of x-ray scattering techniques to this problem.

We have shown that synchrotron radiation combined with a superconducting magnet capable of generating a 13 Tesla field is a very powerful tool to study a particular such 1D magnet, the recently discovered spin-Peierls compound CuGeO_3 . In this system the Zeeman energy corresponding to a ~ 12 T field lowers the energy of the first excited state enough to drive a magnetic field induced transition into an incommensurate (IC) spin-lattice modulated phase.

The nature of this phase is intimately related to the nature of the excitation spectrum and has been the subject of much theoretical work. Prior to our experiments the IC phase had been inaccessible to scattering probes. By measuring first and (weak) third harmonics of the IC superlattice reflections (see Fig. 1) we have shown that the high-field phase is a multisoliton state (soliton lattice) and measured both the intersoliton distance and the soliton width as a function of field and temperature. The resulting magnetic phase diagram, consisting of commensurate, incommensurate, and undistorted phase, is in qualitative agreement with theoretical predictions. In particular, we have confirmed the prediction that the IC phase is reentrant in temperature over a certain field range. However, our data analysis has also revealed some startling quantitative discrepancies with extant theoretical predictions. In particular, the measured soliton width is almost twice as large as predicted. An explanation of our data is a challenge for the theory of 1D quantum magnetism, and we expect significant interest in our work in theoretical community.

Figure 1. Scans through the (3.5, 1, 2.5) superlattice reflection of CuGeO_3 at $T=4\text{K}$ in the Incommensurate phase. Successive scans were multiplied by 100 in order to achieve a constant offset on the logarithmic scale. The lines are the results of fits to resolution-limited Gaussians.

S.D. Kosowsky, P.S. Pershan (Harvard Univ.), K.S. Krisch, J. Bevk, M. Green, L.C. Feldman and P.K. Roy (AT&T Bell Labs)

Specular reflectivity measurements were performed on a series of poly-Si/SiO₂/Si(001) MOS structures, with thin (<100 Å) oxide layers, which are relevant to current microchip technology. The samples consisted of single crystal substrates with SiO₂ layers grown on top. A 2500 Å heavily-doped polycrystalline silicon (poly-Si) layer formed the conducting cap. The devices were prepared at AT&T production and research facilities in Allentown, Orlando and Murray Hill, under different sets of growth and annealing conditions. The goal of this work is to relate structural properties to processing parameters.

Two reflectivities are shown below with the corresponding real space profile derived by fitting the x-ray scattering with a layered model. The two data sets shown are from two identically fabricated MOS capacitors, except that one had a final activation anneal (b) and one did not (a). The reflectivity data, $R(q)$, has been divided by the well-known Fresnel curve, $R_f(q)$, and the corresponding real space fits are also shown below. Several features of the data can be interpreted in a real space model. (1) The steep fall off in the R/R_f for $q < 0.2 \text{ Å}^{-1}$ results from the rough poly-Si/vacuum interface. This interface is 15-50 Å rough (rms), with higher roughness values resulting from higher annealing temperatures. (2) The bump in the R/R_f of the unannealed sample, centered at $q=0.55 \text{ Å}^{-1}$, corresponds to a dense, 5 Å layer at the SiO₂/Si(001) interface. This layer is unstable to high temperature (>800 °C) annealing as it is absent from the annealed sample. (3) The oscillations in the unannealed sample, corresponding to the oxide thickness, are modulated. This modulation implies structure at the SiO₂/poly-Si interface as well, and a diffuse, 3-8 Å layer allows the data to be fit. The absence of modulation in the annealed sample is due to the disappearance of the SiO₂/Si(001) layer upon annealing.

Figure 1. Fresnel normalized reflectivities for two MOS samples, one annealed (b) the other not (a), otherwise prepared identically.

Figure 2. Real space density profiles for the two samples.

O.M. Magnussen, B.M. Ocko (BNL), M.J. Regan, P.S. Pershan (Harvard), M. Deutsch (Bar-Ilan, Israel)

We have previously demonstrated that liquid Hg [1] and Ga [2] exhibit surface induced layering, in accordance with decade old theoretical predictions. Here we present x-ray scattering results on films of organic molecules (alkane-thiols) on the liquid Hg surface. For thiols with hydrocarbon chain lengths between 8 and 18 molecules well-defined mono- and multilayer structures were observed. As an example, the normalized x-ray reflectivity spectrum, R/R_f , from an adsorbed octadecanethiol monolayer on Hg is shown in the figure along with the spectrum from the pure Hg/vapor interface. The interference between the reflected amplitudes from the vapor/thiol and thiol/Hg interfaces gives rise to the observed modulated reflectivity spectrum. The modulation period corresponds to a fully extended alkane chain and the amplitude supports the notion of a densely packed monolayer. Remarkably, the essential features of the reflectivity, including the quasi-Bragg peak and the dip at small q_z , are identical with and without the thiol monolayer. This clearly supports the notion that the surface layering is an intrinsic feature of the Hg surface. For higher dosages of thiols very smooth multilayer structures are formed. Complementary in-plane x-ray diffraction measurements indicated that thiol multilayers are well ordered and are packed in a distorted hexagonal arrangement parallel to the surface plane while no in-plane ordering was observed for thiol monolayers.

[1] O.M. Magnussen et al., Phys. Rev. Lett. 74, 4444 (1995) [2] M.J. Regan et al., Phys. Rev. Lett. 75, 2498 (1995)

Figure 1. X-ray reflectivity (R/R_f) from the clean Hg vapor interface (dashed line) and from an octadecane thiol (18 carbon atoms) terminated Hg surface (circles).

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L. J. Martínez-Miranda (U. of Maryland at College Park)

We have studied the structural evolution as a function of film thickness of films of the room temperature smC* mix mx5112, which has a smA - smC* at 46°C, deposited on 10 μm period gratings. There is a homogeneously aligned layer for films as small as 1 μm thick, which is ten times smaller than the critical thickness observed for similar films of the compound 8CB [1]. The experiments used 9keV x-rays, focused on a spot of 2mm² at the sample position. The detector slits were kept at a 10(vertical)x4(horizontal)mm² opening. We studied the regions of varying smectic layer orientation by changing the value of the angle χ : this scan is equivalent to changing the value of the out of plane component of l in reciprocal space. The diffraction angles $\theta, 2\theta$ are held constant at the Bragg value for mx5112. At $\chi = 0^\circ$, the observed scattering corresponds to smectic layers parallel to the surface of the gratings (molecules perpendicular to the plane of the substrate). Conversely, at $\chi = 90^\circ$, the signal observed corresponds to smectic layers aligned perpendicular to the plane of the substrate (molecules parallel to the plane of the substrate). The nominal angle of incidence α in these runs was 0° . Finally, we performed azimuthal ϕ -scans as well as in-plane Bragg scans at $\chi = 0^\circ$ in order to observe the degree of in-plane disorder. For these scans, $\phi = 0^\circ$ corresponds to the [100] direction.

We have concentrated on the structural evolution of order in mx5112 films of thicknesses ranging between 2 and 15 μm . Films thinner than 10 μm exhibit an evolution of molecular layer spacing as a function of depth within the sample. In particular, the layers closest to the LC-glass interface show a time dependence in azimuthal ordering, with the molecules rotating in the direction of the gratings over a 5- hour period. The LC layers are more smA-like near the LC-glass boundary in this case. The in-plane LC layer spacing stabilizes at an intermediate size beyond a film thickness of 10 μm , while the out-of-plane spacing decreases in the same region. This result suggests that the LC-glass interface pins the layer tilt, leaving the film in a quenched state. A quantitative analysis of these results is in progress at the moment.

In addition to the measurements above, we have studied the LC-glass interface on both a 15 μm mx5112 film as well as a 29 μm 8CB film by performing a reflection scattering study through the surface of a 0.25 mm grated glass substrate, on the air-LC-glass confined system. A comparison with the above results on mx5112 shows consistency in the observations performed through either interface. This part of the project uses the absorption of the xray beam by both glass and the LC to control the penetration depth of the beam through both. This measurement constitutes a very important step in our ability to observe the structure of LC interfaces in prototype LC devices.

[1]. E. Smela and L. J. Martínez-Miranda, J. Appl. Phys., 77, 1923 (1995).

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K.Penanen, P.S.Pershan, M.Regan, and I.F.Silvera (Harvard)

It is well known that free electrons can be held onto the free surface of liquid helium through either their own image charges or through the effect of an externally applied electric field. The resultant electrostatic pressure causes films to thin. We have measured x-ray specular reflectivity from static films of isotopic mixtures of helium with an intense x-ray beam in the temperature range between 0.37 K and 1.3 K. Normally, no significant thickness variation with x-ray intensity is expected over a wide range of temperatures when the film is superfluid. We have found that even modest x-ray intensities affect the thickness of films containing only trace amounts of ^3He . Figure 1 shows the measured ratio R/R_{Fresnel} for a mixture with trace amounts of ^3He at 0.47K for three different intensities. The thickness for small intensities is of order 200 Å, in agreement with the theory and pure ^4He data for higher temperatures taken by Lurio *et al.* At higher intensities the film thins, with poorly defined thickness due to variation of the intensity with the incident angle. At higher concentrations of ^3He the period of the interference fringes becomes irregular and the determination of the film thickness becomes problematic. Figure 2 demonstrates this point. We believe that the effect is due to x-ray produced photoelectrons, which thermalize in the vapor and then reside on the surface, attracted by both the film and a charged substrate. The temperature and concentration dependence is then due to the transport properties of the electrons at the surface. It may be possible to study the 2-D electron gas produced in this way by diffraction techniques.

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Figure 1. X-ray dosage effect on a film containing trace amounts of ^3He

Figure 2. Structure factor as a function of the wave vector transfer $Q = \frac{4\pi}{\lambda} \sin \theta$ for a range of temperatures and bulk ^3He concentrations. The curves were separated by 0.5 for clarity.

P. Sonntag, P. Bodeker, H. Zabel (Ruhr-Universität Bochum, Germany)

We have investigated the magnetic structure of Cr[001] films on Nb/Al₂O₃ with and without a cap layer of Fe. The Cr thickness ranged from 500 to 3000 Å. Via X-ray scattering in the wide angle regime we measured the satellite reflections due to the charge density waves (CDWs) and strain waves (SWs) in the Cr films being second harmonics of the spin density waves which form the antiferromagnetic ground state of Cr. The left part of Fig. 1 displays scans in the L-direction on both sides of the Cr(002) reflection of a 3000 Å thick Cr[001] film on Nb/Al₂O₃ for different temperatures and scans around the Cr(011) reflection performed in the K-direction in the reciprocal lattice of the same sample. The measurements illustrate the strong orientational polarization of the CDW/SW modes which we observed in the sample system Cr[001]/Nb/Al₂O₃. Only modulations with their wave vectors pointing perpendicular to the film plane could be detected [1]. This behaviour may be due to an interfacial pinning effect at the Cr/Nb interface. The investigations of the temperature dependence of the satellite intensities and positions reveal a slight increase of the Néel-temperature as well as an enlargement of the CDW/SW period around the Cr(011) and the Cr(002) reflections at various temperatures are shown in the right part of Fig. 1. Only CDW/SW modes with their wave vectors lying in the film plane can be observed. The Fe top layer appears to favour a transverse in-plane SDW mode in the Cr film with spins pointing perpendicular to the film plane. Concerning the CDW/SW period and the Néel-temperature the same effects as in the Cr/Nb/Al₂O₃ system could be observed. To clarify the origin of the reorientation of the CDW/SW more detailed studies are planned for the future.

Figure 1. Left: CDW/SW satellite reflections of a 3000 Å thick Cr[001] film on Nb/Al₂O₃ at the Cr(002) reflection in the L-direction at various temperatures and at the (011) reflection in the K-direction at 20 K. Right: CDW/SW satellite reflections of a 2000 Å thick Cr[001] film on Nb/Al₂O₃ with a 20 Å thick Fe cap layer at the Cr(011) reflection in the K-direction at various temperatures and at the (002) reflection in the L-direction at 30 K.

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A. Vigliante, J. P. Hill, Doon Gibbs (BNL), V. Kiryukhin, B. Keimer (Princeton)

The origins of the rich magnetic phase behavior of the rare-earths lie in the competition between the indirect exchange interaction of the localized 4f moments, and in an ordering into a basal plane spiral propagating along the c-axis direction at $T_N=132$ K. At lower temperatures the basal plane becomes important and causes the wave-vector to lock-in to various commensurate values, as described by the spin-slip model. Below $T=20$ K, the spins cant out of the plane to form a ferromagnetic spiral phase. Disturbing this balance, by applying a magnetic field, provides a direct experimental handle on the competition and should help to elucidate the nature of the interaction. Indeed, exotic new phases such as helix have been predicted and observed by Neutron Scattering. We have utilized resonant magnetic x-ray scattering to study a number of rare-earths with a field applied in the basal plane, along the easy b-axis. In particular, we have mapped out the magnetic phase diagram of holmium in the region, $90 \leq T \leq 132$, $0 \leq H \leq 7$ Tesla. We find a variety of phases, notably a $2/7$ lock-in, in the vicinity of the Néel transition. In addition, a large increase in the scattered intensity is observed as the field is increased for $43 < T < 98$ (see fig. 1). We tentatively ascribe this to a bunching of the moments along the direction perpendicular to the fields, in the basal plane. At high fields, the intensity abruptly drops at a first order phase transition into a low intensity phase, which is consistent with the formation of a fan phase, with the moments bunching along the field direction. Initial experiments have also been carried out on erbium and dysprosium for which data analysis is ongoing.

Figure 1. Magnetic wavevector τ as function of magnetic field at $T=96.24$ K.

A. Vigliante, J. Tranquada, J. D. Axe, Doon Gibbs, B. Ocko (BNL)

Several Studies on cuprate systems have established that the suppression of the superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ when $x=1/8$, requires both a hole concentration of $1/8$ per Cu and a distortion from the low-temperature-orthorhombic (LTO) to the low-temperature-tetragonal (LTT) structure. One system that is particularly convenient to investigate this phenomena is $\text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{CuO}_4$ with $y=0.4$ and $x=0.12$, due to the coexistence of the $1/8$ hole concentration and the LTT phase. J. Tranquada et al. [Nature 375, 561 (1995)] have found evidence, by Neutron Diffraction, of long-period commensurate ordering of antiferromagnetic stripes separated by charge domain walls in the LTT phase. The magnetic modulation peak associated with the spin stripes order was clearly observed at $(1/2, 1/2 \pm \epsilon, 0)$ with $\epsilon=0.12$. The charge modulation peak associated with the hole stripes order should be essentially two dimensional, with the modulation wave-vectors $(\pm 2\epsilon, 0, 0)$ for the vertical stripe layers and $(0, \pm 2\epsilon, 0)$ for the horizontal stripe layers. The neutron experiment shows the evidence of a peak in the LTT phase at $(0, 2-2\epsilon, 0)$ with $\epsilon=0.12$. The intensity of the observed peak is $\sim 10^{-6}$ that of the strong $(0, 2, 0)$ nuclear reflection. Since Neutron Scattering detects the modulation charge peak indirectly, a complementary X-Ray Scattering experiment was performed to confirm the Neutron results. A small peak, of the order of $\sim 10^{-6}$ with respect to the charge Bragg peak $(0, 2, 0)$, at $(0, 1.76, 0)$ was observed below the LTO-to-LTT transition temperature of $T_c=70\text{K}$. The presence of a high, sample related, background and the two dimensional character of the scattering made this experiment quite difficult and further studies are needed to better quantify this phenomena.

Th. Wandlowski (Ulm), B. M. Ocko, O.M. Magnussen (BNL Physics), W. Wu, J. Lipkowski (Guelph)

In-situ x-ray scattering studies of the Au(111) electrode surface have been carried out in KClO_4 solutions containing uracil, pyridine or 2,2'-bipyridine using grazing incidence angle diffraction. At sufficiently negative potentials the $(\sqrt{3} \times \sqrt{3})$ surface reconstruction forms with a stripe separation $p = 23$. The formation of a two-dimensional condensed uracil film or a complete monolayer of planar-oriented pyridine or 2,2'-bipyridine hinders the lifting of the reconstruction. Whereas the stripe separation increases continuously over a 0.6V range, in the base electrolyte the presence of the organic compounds blocks this process considerably. Only a small, step-like increase in p is observed, where the adlayer is disordered. There exists a 0.7V hysteresis between the lifting and the subsequent formation of the reconstruction. The $(\sqrt{3} \times \sqrt{3})$ phase reappears at potentials where a gas-like adlayer is formed again. Cyclic diffractograms and potential step measurements have been employed to study the time dependence of this substrate transitions for the system uracil/Au(111). The kinetic studies demonstrate that the substrate surface reconstruction/deconstruction kinetics follow nucleation-and-growth-based mechanisms. The lifting of the reconstruction in the presence of uracil proceeds in two steps, which involve the disintegration of the $(\sqrt{3} \times \sqrt{3})$ phase and the transformation of a disordered surface structure into an ordered (1×1) phase. The potential-induced reconstruction can be described by an Avrami-type formalism with exponents ranging between 1.9 and 2.3.

Figure 1. Cyclic Voltammogram for uracil and stripe separation for some organics on Au(111).

Figure 2. Time dependence of the (0,1,0.2) intensity after application of a potential step from either -0.8 V (A) or 0.70 V (B) to various final potentials.

The effects of hydrogen adsorption/evolution and bisulfate coadsorption on the structure of underpotentially deposited Tl adlayers on Pt(111) *

X22A,
X22B

J.X. Wang, R.R. Adzic (BNL/DAS), B.M. Ocko, O.M. Magnussen (BNL/Physics)

Tl forms an incommensurate, aligned-hexagonal phase in acid and alkaline solutions at the most negative potentials prior to its bulk deposition or hydrogen evolution. The monolayer compresses, thus the Tl coverage increases, with decreasing potential. In acid solutions, this phase exists in the potential region where hydrogen adsorption and evolution occur in the absence of Tl^+ (Fig. 1). Underpotential deposition (UPD) of Tl suppresses hydrogen adsorption but does not shift the onset of hydrogen evolution. On the other hand, the competition of Tl UPD with hydrogen adsorption/evolution causes a slightly lowering of Tl coverage and a significant decrease of the in-plane ordering of the Tl monolayer.

In sulfuric acid solution, a $(\sqrt{3} \times \sqrt{3})R30^\circ$ diffraction pattern was observed over a 0.28 V wide potential range, which corresponds to the potentials between the two major peaks in the voltammogram. The involvement of both Tl and anion species in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice structure can be inferred from the absence of the diffraction signal in the solutions without either Tl^+ or bisulfates. Specular reflectivity data support the model with $1/3$ monolayer of Tl at the hollow sites. It is, however, difficult to determine, directly from surface x-ray scattering, the bisulfate coverage and its adsorption sites. The similarity of bisulfate adsorption (without Tl) and coadsorption (with Tl) features in the voltammograms and the positive potential shift in the latter case suggest that bisulfate coadsorption is primarily through the interaction between bisulfate and Pt. This leads us to the model with bisulfates coadsorbing at the hollow sites of the Tl adlayer. In the top view picture shown in Fig. 1, Tl, Pt, S, and O are represented by the circles with the diameters corresponding to their relative atomic sizes. It can be seen that the model gives adequate interatomic spacings.

Figure 1. Tl coverages in the aligned-hexagonal (circles) and the $(\sqrt{3} \times \sqrt{3})R30^\circ$ (triangles) phases as a function of E and voltammograms in 0.05 M H_2SO_4 solutions with (solid line) and without (dashed line) 5mM Tl^+ . Sweep rate 20 mV/s.

* This work is supported by the DOE, contract DE-AC02-76CH00016

X-Ray Study of Orientational Correlations in C_{60} above 260K *

X22B

P. Wochner, J.D. Axe (BNL), P.C. Chow, S.C. Moss (U. of Houston), J.W. Dykes, S.H. Irons, J.Z. Liu, R.N. Shelton (U. of California, Davis)

Premonitory orientational fluctuations above the first order phase transition of C_{60} at 260K have been studied by diffuse X-ray scattering experiments. These experiments probe the orientational pair correlations between C_{60} molecules as a function of their separation and therefore the orientational potential. In addition to the diffuse scattering due to the orientational disorder of single molecules, we have observed zone boundary diffuse scattering at the X-points related to the $\text{Pa}\bar{3}$ low temperature structure up to 300K (Fig. 1). An additional set of diffuse peaks, which are even at room temperature comparable in intensity to the former ones, have been found at (0.5,0.5,0.5) positions (L-point) (see Fig. 1). Similar results have recently been reported by P. Launois et al. [1] and L. Pintschovius et al. [2]. The temperature dependence of the integrated intensity of both sets of diffuse peaks shows only a weak increase in approaching T_c , indicative of a strongly first order transition. Additional intensity with a very weak temperature dependence but similar correlation length has also been found at (0.5,0.5,0) and (0.5,0,0) positions. The diffuse intensity at the L, Σ and Δ points has probably its origin in competing phases which are not stabilized at low temperatures. The analysis of the data using orientational model potentials is in progress and will be a good test for all the theoretical models predicted so far.

[1] P. Launois, S. Ravy, R. Moret, Phys. Rev. B 52, 5414 (1995)

[2] L. Pintschovius, S.L. Chaplot, G. Roth, G. Heger, PRL. 75, 2843 (1995)

Figure 1. Contour plot of diffuse intensities in the (110) reciprocal lattice plane centered on the (236) $\text{Pa}\bar{3}$ reciprocal lattice point. The X-point at (236) and the L-points at (2.5,2.5,5.5) and (1.5,3.5,5.5) are marked by a dot and a square, respectively. The apparent shift of the diffuse maxima away from these positions is due to the strongly Q-dependent background from Laue-scattering off the single C_{60} molecules.

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The Magnetic Structure of $\text{GdNi}_2\text{B}_2\text{C}$ by Resonant and Non-Resonant X-Ray Scattering *	X22C
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C. Detlefs, A. I. Goldman, C. Stassis, P. C. Canfield, B. K. Cho (Ames Lab), J. P. Hill, and D. Gibbs (BNL)

Resonant and non-resonant X-ray magnetic scattering techniques have been used to study the low temperature magnetic structure of $\text{GdNi}_2\text{B}_2\text{C}$.

As the temperature was lowered below 19.4 K, the Néel temperature, magnetic scattering developed as satellites of the charge peaks at $(h \pm q_a, k, l)$ with q_a ranging from 0.550 to 0.553 over the temperature range studied. As shown in fig. 1, the low temperature ($T \leq 13.6$ K) scans of the $(2 - q_a, 0, 0)$ peak taken at the Gd L_2 energy exhibit a strong resonant scattering contribution. Above approximately 13.6 K, however, the resonant enhancement of the magnetic scattering is essentially absent (see fig. 1e) so that the intensity and line shape of the magnetic scattering observed at the Gd L_2 edge is comparable to the non-resonant data set taken at 7.0 keV. The non-resonant magnetic scattering persists up to the Néel temperature.

The cross sections for the resonant and nonresonant magnetic scattering show that the absence of significant resonant scattering at the magnetic wave vector between 13.6 K and 19.4 K, and the presence of non-resonant scattering imply that, in this temperature region, the ordered moment is oriented in the basal plane and transverse to the modulation wave vector (e. g. $\mathbf{M} \parallel \mathbf{b}$ for the a-axis modulation), as was found for $\text{ErNi}_2\text{B}_2\text{C}$ by neutron diffraction. Below 13.6 K, however, the observation of resonant enhancement implies that an ordered component of the moment exists in the scattering (a,c)-plane.

In order to determine, more precisely, the direction of the moment below 13.6 K, we have carefully measured the integrated intensity of a series of satellites along the a^* -axis both on and off the resonance condition at the lowest temperature accessible (3.5 K). From these measurements, we deduce that below 13.6 K the moment remains transverse to the propagation direction and acquires a component out of the basal plane.

Figure 1. The results of fits to the complete data set obtained from the non-resonant (a,b,c) and resonant (d,e,f) measurements showing the evolution of position, intensity and width of these peaks.

* Work supported by DOE DE-AC02-76CH00016.

Charge Density Waves in Doped Chromium *	X22C
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J.P. Hill and B.J. Sternlieb (BNL)

The $[\text{Ar}]3d^5 4s^1$ electronic configuration and bcc crystal structure of pure chromium metal results in a band structure whose major components in reciprocal space are an electron octahedra at the zone center, Γ and a somewhat larger hole octahedra located at the corners, H , of the Brillouin zone. Large portions of the Fermi surface can then be "nested" via an incommensurate wave-vector $\mathbf{Q}_{\pm} = (1 \pm \delta, 0, 0)$. As a result, a linear spin density wave (SDW) forms below the Neel temperature $T_N = 311\text{K}$, accompanied by a charge density wave (CDW) of twice the wave-vector. These phenomena are exquisitely sensitive to electron density. Doping with electron donors, such as manganese or rhenium increases the size of the electron pocket and drives the system towards commensurability. While the SDW in doped systems has been much studied, in particular by neutron scattering, the CDW has not yet been observed. X-rays are particularly well matched to the study of CDW's and we have therefore carried out a preliminary study of $\text{Cr}_{0.993}\text{Mn}_{0.007}$. We find that as in pure chromium there is a CDW of twice the wave-vector of the SDW observed by neutron scattering. In fig. 1 we show a scan taken along the $(H00)$ axis which displays two satellites of the (200) Bragg peak, corresponding to the two choices of nesting vector. In addition, we observe a second harmonic to the CDW which implies that the modulation is not sinusoidal.

This in turn implies that the SDW is not sinusoidal either. Similar behavior has been previously seen in pure chromium. Interesting questions for future work include a study of the temperature dependence of the harmonics which will provide information on the coupling of the CDW to the SDW, and a high resolution study of lineshape widths to elucidate pinning effects.

Figure 1. Longitudinal Scan at $T=14$ K showing CDW with 2 harmonics.

* Work supported by DOE DE-AC0276CH00016

Incommensurate Antiferromagnetism in the Intermetallic Superconductor $\text{HoNi}_2\text{B}_2\text{C}$ *

X22C

J.P. Hill, B.J. Sternlieb, D. Gibbs (BNL), C. Detlefs, A.I. Goldman, C. Stassis, P.C. Canfield and B.K. Cho (Ames Lab. and ISU).

Superconductivity arises from the Bose condensation of Cooper pairs; a pairing of electrons of opposite momenta and spin. In most superconductors even dilute concentrations of paramagnetic impurities suppress T_C , or destroy the superconductivity completely. However, for antiferromagnetic order the competition is less direct and the two ground states can, in principle, coexist microscopically. Interest in this competition has been reawakened by the discovery of a new class of magnetic superconductors, $\text{RNi}_2\text{B}_2\text{C}$. These have superconducting transition temperatures, T_C as high as $T_C=16.6\text{ K}$ (for $R=\text{Lu}$) and Néel temperatures as high as $T_N=10.3\text{ K}$ (for $R=\text{Dy}$). The antiferromagnetism is characterized by a rich variety of phases among the different members of the series, including simply commensurate and incommensurate structures.

We have carried out a study of the magnetic phase behavior of $\text{HoNi}_2\text{B}_2\text{C}$ ($T_C=8.5\text{ K}$, $T_N \approx 7\text{ K}$), utilizing resonant magnetic x-ray scattering. This compound exhibits a large reduction, or extinction, of the superconducting order parameter in the incommensurate antiferromagnetic phase. We find that at low temperatures, $T < 5\text{ K}$, the superconductivity coexists with a well ordered, commensurate Néel state with a correlation length of $\approx 5300\text{ \AA}$.

In the incommensurate antiferromagnetic state, $5\text{ K} < T < 7\text{ K}$, we find two phase coexistence between an a-axis modulation and a c-axis basal plane spiral. Fig. 1 shows a scan along the (00L) direction in the vicinity of the (003) position, taken in the incommensurate phase. Surprisingly, the c-axis structure is characterized by two wave-vectors. One of these modulations is extremely well ordered, with correlation lengths well in excess of $5000\text{ \AA}$ while the other is more disordered, $\xi = 600\text{ \AA}$ at $T=5.4\text{ K}$. In addition, short range ordered fluctuations of the commensurate phase, observed for $T > 5\text{ K}$, are present above T_{C-IC} . We believe that these are the result of local strains.

Figure 1. L Scan in the vicinity of the (003) antiferromagnetic reciprocal lattice position

* Work supported by DOE W-7405-ENG-82.

Observation of x-ray magnetic scattering in Nd_2CuO_4 *

X22C

J.P. Hill, A. Vigliante, D. Gibbs (BNL), J.L. Peng and R.L. Greene (U. Maryland)

In order to develop a comprehensive understanding of the high T_C superconductors, it is useful to study the parent compounds to characterize the underlying insulating state from which the superconductivity develops. Of particular interest are their magnetic properties, and here common features are seen in La_2CuO_4 , the progenitor of the hole doped superconductors, and Nd_2CuO_4 and Pr_2CuO_4 , the precursors of electron carrier superconductivity. There are, however, some important differences, including the presence of the rare-earth ions in the electron superconductors. These ions carry localized 4f moments, which can themselves order. In this work, we report a study of Nd_2CuO_4 , utilizing resonant x-ray magnetic scattering. The main advantage of this technique is the possibility of separating the ordering of the Nd moments from that of the Cu moments by tuning the incident energy to a Nd absorption edge. In addition, high spatial resolution offers the possibility of examining mesoscopic length scales.

The experiments were performed by tuning the incident energy to the Nd L_I , L_{II} , and L_{III} absorption edges. The largest count rates, up to 300 counts per second, were obtained at the L_{II} edge. Antiferromagnetic long range order is seen below $T_{Nd} = 37\text{ K}$. The Bragg peaks are resolution limited, corresponding to correlation lengths of $\xi_{aa} \geq 2300 \pm 100\text{ \AA}$ in the plane and $\xi_c \geq 7500 \pm 400\text{ \AA}$ perpendicular to the plane. Polarization analysis confirms that the scattering is magnetic in origin and consistent with a dipole excitation, suggesting that the Nd 5d bands are polarized. In fig. 1 the intensity of the (0.5, 0.5, 8) magnetic Bragg peak is plotted as a function of temperature. There is no appreciable ordered Nd moment above $T \approx 37\text{ K}$. At low temperatures the ordered moment is seen to rise rapidly. These results confirm earlier interpretations of neutron-scattering data.

Figure 1. Magnetic Bragg peak intensity as a function of temperature. Solid line is a guide to the eye.

* Work supported by NSF DMR 9209668

S. Langridge (ESRF, EITU), G.H. Lander (EITU), N. Sato (U. Sendai), and D. Gibbs (BNL)

The aim of this experiment was to examine the critical scattering in the heavy-fermion compound UPd₂Al₃. The crystal, which had previously been examined by neutrons, was polished but not annealed. A mirror finish was apparent to the eye. The mosaic FWHM=0.12°. Magnetic scattering of $\approx 15,000$ cts/sec was observed at the (0,0,1.5) reflection below T_N . The results of the experiment provide (probably) little information about the intrinsic properties of UPd₂Al₃, but new insight into the "two-length scale" problem. Two figures of the "raw data" are given below, both from scans of the (0,0,1/2) reflection.

Figure 1 shows the decrease of intensity with T . Note especially the linear T scale. Scattering can still be seen at a reduced temperature $t = 0.35$, which is highly unusual. The width of this scattering increases considerably, also approximately linearly on semilog scale, but the extracted widths depend on the fits to the data.

Figure 2 shows the change of the position of the center of the antiferromagnetic (0,0,0.5) peak as a function of T . Over this range the "apparent" c -axis changes by $\approx 0.6\%$. In fact, the bulk c -axis spacing does not change, but the material giving rise to the magnetic "critical" scattering exhibits a change in d -space. More likely, this represents a change of T_N at the surface and the changing width is related to the particle size. TEM studies are now in progress to characterise the surface. Different fitting procedures are also under consideration.

Figure 1. Decrease of intensity with T for the (0,0,1/2) reflection.

Figure 2. Change of position in L of the centre of the magnetic scattering as a function of T .

S. Langridge (ESRF, EITU), G.H. Lander (EITU), Y. Yamaguchi (IMR), and D. Gibbs (BNL)

The resonant magnetic scattering involving dipole matrix elements contains higher-order terms that give additional information on the resonant matrix elements involved in the scattering process. Such higher-order terms have been observed [1] in the $2p \rightarrow 5d$ L resonances of holmium metal, but not yet from the dipole M resonances in uranium involving a $3d \rightarrow 5f$ transition. This is unusual in view of the fact that the enhancements for first-order harmonics at the M resonances are much stronger than at the L resonances. However, the interference conditions for observing the higher-order terms are stringent. The moment configuration must not be collinear otherwise the geometric term will be zero [2]. Therefore, the best configuration is a spiral (as in Ho). Such a magnetic structure is difficult to find in uranium compounds; but we have tried the experiment on a single crystal of orthorhombic UPtGe. Following neutron investigations this material has a cycloidal structure propagating in the [010] direction with the spins in the bc plane [3,4]. This configuration, if correct, allows a 2^{nd} order peak from the M-resonance (i.e. it is not geometrically forbidden), and, because the magnetic propagation vector is incommensurate, $q = [0, 0.551, 0]$, the $2q$ peak should be observable.

The crystal used was polished and gave a mosaic of 0.2° . Cooling below T_N (≈ 51 K), we found the (0, 1.4487, 0) peak of 700 cts/sec. This was disappointingly small, partly because of the relatively poor mosaic. Interestingly the transition at T_N is continuous ($\beta = 0.32$) which in an orthorhombic system implies a 1-dimensional order parameter. This is clearly not consistent with the previous neutron data [3,4].

Searches for the $2q$ peak failed to find any measurable intensity, $< 1\%$ of the q peak. A simple calculation assuming a bc plane spiral with equal uranium moments predicts a ratio of $\approx 15\%$. Since the ratio $2q/q$ in Ho is $\approx 4\%$, this ratio is surprisingly low in the M_{IV} U resonance. Unfortunately, this conclusion is correct only if the magnetic structure is known. The neutron study also considered a transverse linear wave rather than a cycloid, although with a poorer "goodness of fit" for this model. This transverse wave would give no $2q$ satellite. Further study of this problem by neutrons and X-rays is planned to evaluate which of these alternatives is correct in the above interpretation.

- [1] D. Gibbs et al. Phys. Rev. B 43, 5663 (1991)
- [2] J. P. Hannon et al., Phys. Rev. Lett. 61, 1245 (1988)
- [3] S. Kawamata et al. JMMM 104-107, 51 (1992)
- [4] R. A. Robinson et al. Phys. Rev. B 47, 6138 (1993)

S. Langridge (ESRF), J.A. Paixão (U. Coimbra), G.H. Lander (EITU) and D. Gibbs (BNL-Physics)

DyFe_4Al_8 has the tetragonal body centred structure of ThMn_{12} . In the RFe_4Al_8 ($\text{R}=\text{Actinide}$ or rare-earth) systems almost all the Fe atoms sit on the $8(f)$. This allows a study of both the transition metal and rare-earth sublattices and of the interactions between them. From neutron and transport property studies [1] the Fe atoms are known to order at $\approx 175\text{K}$ with a temperature independent wave-vector of $\tau=(0.133,0.133,0)$, close to the commensurate value of $2/15$. At approximately 35K the Dy atoms order with the same magnetic wave-vector. The magnetic structure is complex and not completely characterised. Using a polished single crystal (with a mosaic width of 0.04°) resonant magnetic x-ray scattering was observed at the Dy L_{III} resonance ($E=7.79\text{keV}$). Representative scans are shown in figure 1 around the (220) and (330) charge peaks. Around the (220) charge peaks symmetric satellites were observable at the $\pm\tau$ and $\pm 2\tau$ positions. The energy and temperature dependence of the $\pm\tau$ peak show that it is magnetic in origin whilst the $\pm 2\tau$ peaks arise from a displacement of the Fe atoms. The crystallographic symmetry is such that only the Dy atoms contribute to the scattering around the odd satellites (lower panel in figure 1). No scattering was observed at the 3τ position. Following the superlattice peaks as a function of temperature (figure 2) it is clear that a signal exists at the $(3\pm\tau, 3\pm\tau, 0)$ position up to $\approx 110\text{K}$. Resistivity and susceptibility measurements also indicate an anomaly in this temperature range [1]. The scattering is also strongly energy dependent. Since electric dipole contributions usually dominate the enhanced magnetic scattering we can speculate that the scattering is a result of the polarisation of the $5d$ conduction electrons by the Fe field. Below 30K there is a large enhancement in the magnetic signal corresponding to an increase in the ordered Dy moment consistent with neutron and Mössbauer measurements [2, 3]. Similar effects have been observed in a Nd high T_C parent compound [4]. Neutron scattering experiments are scheduled to define the magnetic moment direction and further x-ray studies of the polarisation and temperature dependence of the superlattice peaks (and harmonics) aim to identify the origin of the high temperature scattering.

[1] Buschow and van der Kraan, J. Phys. F 8 (1978) 921.; [2] Paixão and Lebech. Private communication (1995).; [3] Gubbens et al. J.M.M.M. 27 (1982) 61.; [4] Hill et al. submitted to Phys. Rev. B.

Figure 1. The superlattice peaks around the (220) (Top) and (330) (Bottom) charge peaks at $T=9\text{K}$, $E=7.79\text{keV}$.

Figure 2. Temp. dependence of the superlattice peaks. Inset shows the intensity which exists above the Dy ordering temp. ($\approx 35\text{K}$).

A. Vigliante, J. P. Hill, Doon Gibbs (BNL), M. J. Christensen, D. F. McMorrow (RISO), G. Helgesen (IFE), R. A. Cowley, M. R. Wells, R. C. C. Ward (Oxford)

Rare earth elements have very similar physical, chemical and electronic properties which allows an almost complete solubility, but very different magnetic structure. Appropriate choices of rare-earth elements based on ordering temperature, anisotropy and controlled growth parameters by Molecular Beam Epitaxy, can tailor the magnetic phase behavior of alloys. We report a quantitative X-ray magnetic scattering study of the magnetic phase behavior of HoPr site-random alloys, as function of concentration. The heavy rare-earth Ho exhibit antiferromagnetic order below $T_N=132\text{K}$, forming a basal-plane spiral with a propagation vector along the c-axis of the hcp structure. In contrast, the light rare-earth Pr, crystallizes in a double hcp structure (dhcp) and is antiferromagnetic only below $T_N=0.05\text{K}$. Magnetic order in Pr can be achieved by in-plane uniaxial stress or by alloying. Chemical and magnetic structural characterization of samples, in concentration ranges of $20\% < \text{Ho} < 80\%$, were studied. The correspondent phase diagram and the temperature dependence of the magnetic wave-vectors are shown in Figure 1 and Figure 2. By allowing the Ho concentration to vary, the chemical structure changes from hexagonal close-packed, to Samarium structure and to double hexagonal close-packed. These changes in the chemical lattice are followed by striking changes in the magnetic structure and in the low-temperature lock-in transformations. X-ray resonant magnetic scattering was performed to isolate the magnetic ordering on the Ho and Pr atoms separately, by tuning the energy to the Ho L_{III} and the Pr L_{III} edges, and to measure the induced moment on the Pr atoms as function of concentration.

Figure 1. Magnetic Phase Diagram of HoPr random thin film alloys.

Figure 2. Magnetic wavevector τ as function of temperature.

Glancing-Incidence X-Ray Magnetic Scattering Studies of the UO_2 (001) Surface	X22C, X25
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G. M. Watson, Doon Gibbs (BNL), G.H. Lander, H. J. Matzke (EITU), B.D. Gaulin (McMaster), L.E. Berman (BNL) and W. Ellis (SNL)

Traditionally, x rays have been used as a probe of the atomic structure in condensed matter. As was first shown by de Bergevin and Brunel[1], x rays can also be used to study magnetic structures. However it is the enhancement of the magnetic scattering cross section when the incident photon energy is tuned to an absorption edge that has made x ray scattering an especially useful probe of magnetic structures. Here we present the first resonant x-ray scattering measurements of the magnetic structure near an interface, obtained under glancing-incidence conditions.

In Figure 1, the scattered intensity along the (10L) magnetic truncation rod of the (001) surface of the simple antiferromagnet UO_2 is shown. Data was obtained with the incident x ray energy tuned to the $U\ M_{IV}$ edge at 3.728 keV. The line indicates the best fit to a model consisting of the ideal, bulk-truncated, magnetic structure, and includes Fresnel effects. We find that the scattering shown in Fig. 1 exhibits an enhancement when the incident photon energy is tuned to the resonant condition, as expected. Remarkably, scattered intensity at grazing-incidence appears to continuously vanish at the bulk Neel temperature. This is in contrast to the bulk magnetic order which is strongly discontinuous.

[1] F. de Bergevin and M. Brunel, Phys. Lett. 39A, 141 (1972).

Figure 1. Intensity of the (10L) magnetic truncation rod measured at three temperatures below the bulk Neel temperature of 30.2 K. Inset: Transverse scan through the (10L) rod at $L = 0.06$.

X-Ray Scattering Studies of Vicinal Au(001)	X22C
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G.M. Watson, Doon Gibbs (BNL), D.M. Zehner (ORNL), Mirang Yoon and S.G.J. Mochrie (MIT)

The focus of this study is to examine the relationship between the structure and morphology of vicinal or stepped surfaces and the structure of the near-by low index surface. For example, it has been found that the faceting and reconstructions observed on stepped Pt(001) surfaces is intimately related to the phase behavior of the step-free surface.[1] In this work, the structure of a stepped Au(001) surface, miscut 1.7 deg towards [110] has been studied between 700 and 1250 K.

Our results are summarized in the experimentally-determined orientational phase diagram shown in Fig. 1. For temperatures above $T^* = 1170K$, the surface is aligned to the macroscopic surface normal. It is believed that at these temperatures the tilted surface is disordered, as was found for the (001) orientation.[2] On cooling below T^* , the surface is observed to phase separate into two distinct orientational phases: hexagonally-reconstructed, step-free (001) facets and a tilted phase. On further cooling to below 990 K, the tilted phase is replaced by a magic vicinal phase. This phase is reconstructed with 3 corrugation periods on each terrace between monoatomic height steps.

[1] G.M. Watson *et al.*, Phys. Rev. Lett. 71, 3166 ('93); M. Yoon *et al.*, Phys. Rev. B. 49, 16702 ('94).

[2] B.M. Ocko *al.*, Phys. Rev. B 44, 6429 ('91).

Figure 1. Orientational Phase Diagram for Au(001) miscut towards [110].

The surface structure of cadmium selenide nanocrystallites as determined by EXAFS, FTIR, and elemental analysis	X23A2
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A.C. Carter (NRL), M.I. Bell (NRL), K.M. Kemner (NRL), C.E. Bouldin (NIST), J.C. Woicik (NIST), S.A. Majetich CMU)

Extended x-ray absorption fine structure (EXAFS), fourier transform infrared absorption (FTIR), and elemental analysis were used on a variety of CdSe nanocrystallites (NC's) in order to study their surfaces. All CdSe NC's were grown by standard microemulsion techniques. Two sets of NC's samples were made. One set was made so that only the size of the NC's were varied, while the surface treatment was kept the same. The other set was made so that only the surface treatment was varied, while the size distribution was kept the same. For the EXAFS experiments, reference compounds were made so that differential measurements could be made, reducing the ambiguity of analysis. FTIR was found to be an excellent probe of the local environments of the surface Cd and Se atoms. The surface Cd atoms are passivated by pyridines and perchlorate groups. EXAFS was able to confirm the existence of perchlorate groups attached to the surface Cd atoms. Elemental analysis also supports the existence of Cl in the samples. The lack of any SeO and SiMe₃ in the FTIR signal indicates that the surface Se atoms are bare. Fourier filtered first shell EXAFS spectra indicate that the only thing bonding to Se in the NC samples is Cd with a reduced coordination number from the bulk, suggesting surface Se atoms are bare. This indicates the existence of many Se lone pair orbitals that can trap an excited hole.

EXAFS Study of Co/X Multilayers	X23A2
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M. Franklin and R. Loloee, Michigan State University

Metallic multilayers involving Co produce a wide variety of magnetic effects and a mixture of structures. Co/Cu and Co/Ag are giant magneto-resistance (GMR) systems for which a mixture of FCC and HCP structures is often claimed. Co/Pd has a change in magneto-anisotropy as layer thickness increases and Co/Mo is a system with conflicting claims about structure. We have begun fluorescence EXAFS studies for these systems with the Co layer thickness fixed at 2 monolayers (ML) as a means of testing the effects of structure upon magnetic properties.

With these artificially layered samples, the choice of a suitable standard becomes a problem. We have chosen data for pure Co metal as a standard which can be used to identify trends reliably. Initial results for our samples have produced one confirmation of results obtained for thicker layers and two features requiring further study. Confirmation. An earlier study of Co y ML/ Ag 17 ML samples indicated the apparent coordination number of the first shell for Co decreased from 12 to 8 as y decreased from 17 to 3 while the saturation magnetization remained essentially constant [1]. The 2 ML Co results are consistent with those results. Feature1. A number of earlier studies [2,3] for thicker Co/Cu samples agreed that the coordination number for Co remained constant at 12 and that it was not possible to distinguish between Co and Cu atoms in that first shell. However, initial results for Co 2 ML/Cu y ML have the coordination number increasing monotonically by 20 increases from 3 to 17. The Debye-Waller and R(NN) values do not change significantly from values found for the thicker samples and thus this increase is not a simple correlated parameter change. Feature2. The EXAFS signals in Co/Mo and Co/Pd samples with 2 ML Co layers have a qualitative change in their form: The signals appear to be a smoothly decaying single frequency. This changes suggest local disorder. XRD data for Co/Mo also indicates disorder and magnetism is lost. XRD data for Co/Pd indicates good long range order and magnetism is not lost. We are varying our analysis procedures to find a reliable quantitative measure of the local disorder in these samples.

[1] C. L. Foiles, et al. MRS Symp. 307,149 (1993). [2] S. Pizzini, et al., Phys. Rev. B 47, 8745 (1993). [3] C. L. Foiles, et al., MRS Symp. Proc. 375,207 (1995).

XAFS Studies of MnSe/ZnTe Superlattices

X11A,
X23A2

A. J. Kropf, B. A. Bunker, J. K. Furdyna, Q. Lu (Notre Dame), and K. M. Kemner (NRL)

Polarization dependent XAFS, employing the total electron yield (TEY) and energy discriminating fluorescence detection techniques, has been used to study the structure of MnSe/ZnTe (001) superlattices grown by MBE. These superlattices consist of 100-300 periods of A/B layers with A and B ranging between 4 and 25 monolayers. Neutron scattering data on these materials show an unique anti-ferromagnetic helimagnetic phase at low temperature which is tunable by varying the thickness, temperature and strain of the MnSe layer (T. M. Giebultowicz, et al., Phys. Rev. B (Rapid Comm.) 46, 12076, 1992).

Of particular interest is the interface between the magnetic MnSe layers and the ZnTe layers, which act as a non-magnetic buffer, magnetically isolating the individual MnSe layers, and the effect of the interface on the strain in the MnSe layers. Polarization dependent XAFS taken at different edge energies coupled with x-ray diffraction results can distinguish between different models of the structure at the interface.

In the data shown below, one can clearly see the effect of the lattice mismatch between MnSe and ZnTe as the MnSe bonds bend, while stretching only minimally, to accommodate the ZnTe lattice spacing. This reduces the first shell amplitude of the the XAFS for x-ray polarization vector perpendicular to the plane of superlattice growth relative to the amplitude of the XAFS for the polarization vector in the plane of the superlattice layers.

Figure 1. Mn Edge Fluorescence Data (Sample 900622A)

XAFS Investigation of Thermal Structural Disorder at GaSb/AlSb Superlattice Interfaces

X11A,
X23A2

Q. Lu, B. A. Bunker, A. J. Kropf, S. W. Short, S. H. Xin, J. K. Furdyna (Notre Dame)

Although surface melting is now well established, the comparable effect at internal interfaces has not been studied to anywhere near the same extent. As part of a larger program to study interfacial properties, we have studied GaSb/AlSb superlattices using X-ray Absorption Fine Structure (XAFS) with total electron yield (TEY) detection. These Ga K-edge measurements have focussed on thermal vibration amplitudes as a function of temperature, polarization, and GaSb layer thickness (either 20Å or 40Å). In XAFS measurements, the thermal vibration amplitude is reflected in the relative radial Debye-Waller (DW) factor, which may be probed as a function of angle and therefore probe in-plane and out-of-plane atomic correlations separately.

The measurements show that the DW factor of Ga at the GaSb/AlSb superlattice interface is much higher in the perpendicular direction than in the parallel direction. This anisotropy increases with temperature and decreases with GaSb layer thickness, and for a pure GaSb film the anisotropy is negligible. The experimental results also shown that the DW factors in the parallel direction are similar between GaSb(40Å)/AlSb(40Å) and GaSb(20Å)/AlSb(40Å), but in the perpendicular direction the DW factor of the GaSb(20Å)/AlSb(40Å) is much higher than that of the GaSb(40Å)/AlSb(40Å). Although this is not direct evidence, this strongly suggests that the interface initiates the melting process.

X-ray Study of Atomic Correlations in ZnCdSeTe Epitaxial Thin Films	X11A, X23A2
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Q. Lu, B. A. Bunker, H. Luo, A. J. Kropf, K. M. Kemner, J. K. Furdyna

X-ray Absorption Fine-structure Spectroscopy (XAFS) have been performed at approximately 90K to study the local structure of thin films of the II-VI quaternary alloy $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{Se}_{0.5}\text{Te}_{0.5}$. Samples were grown by molecular beam epitaxy (MBE) on (100) GaAs substrates, 4° miscut towards the (111)*B* direction with a ZnTe buffer layer. The XAFS data indicate that there are more Zn-Se and Cd-Te bonds in the alloy than expected for a random arrangement. The results imply the formation of high-strain local structure and indicate that electronic pairing energies dominate over strain energy. These results are similar to the earlier observation of interlayer switching in ZnTe/CdSe superlattices. Although no long-range ordering is observed in our room-temperature diffraction measurements, the preference of Zn-Se and Cd-Te bonding also implies a tendency to spontaneously form a composition-modulated microstructure.

XANES study of Cr dopants in oxides	X23A2
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K. E. Miyano (Brooklyn College), J. C. Woicik (NIST), D. Huang (Brooklyn College), Sujaatha Devi, and H.D. Gafney (Queens College)

The presence of Cr^{4+} in Cr-doped Mg_2SiO_4 (forsterite) is critical to the lasing of this material. Other promising Cr-doped oxides are presently being synthesized, and the oxidation state of the dopant Cr atoms is always a critical parameter. X-ray Absorption Near Edge Structure (XANES) data were recorded at the Cr K edge for Cr dopants in Mg_2SiO_4 , NaAlO_2 , and SiO_2 in order to evaluate the Cr oxidation state. Transmission and fluorescence spectra were acquired using the Si (311) double-crystal monochromator, ion chambers, and a Lytle fluorescence detector equipped with a vanadium filter.

XANES spectra were collected from the following standards: Cr metal, CrCl_2 , Cr_2O_3 , CrO_2 , and CrO_3 as standards for the 0, 2+, 3+, 4+ and 6+ oxidation states of Cr, respectively. The Cr-doped NaAlO_2 samples yield a near edge spectrum that is clearly indicative of the Cr^{6+} oxidation state. Although optical measurements have signalled the presence of Cr^{4+} in NaAlO_2 upon synthesis, this measurement indicates that the Cr is susceptible to further oxidation with time. The doped Mg_2SiO_4 samples, on the other hand, are known to have stable Cr. Our initial attempts to interpret the spectra from these samples focussed on the strong preedge peak, which appears in the spectra for higher oxidation states. Also, in the XANES from the standards, the position of the main absorption edge, determined from the peak in the first derivative of the spectra, is observed to have a direct variation with oxidation state. In light of this dependence, analysis of the edge position in the forsterite compound suggests that the Cr in this sample exists in several oxidation states.

Microstructural control of the pore and grain size evolution in silicon nitride during processing.

X23A3

A.J. Allen, G.G. Long, S. Krueger, J. Wallace (NIST), and C.J. Hwang (Dow)

Ultra small-angle x-ray scattering (USAXS) was combined with multiple small-angle neutron scattering (MSANS) to study the microstructural evolution during sintering of the technologically important structural ceramic silicon nitride. USAXS studies utilized maximum entropy (MaxEnt) size distribution analysis to determine volume-weighted pore size distributions during late sintering. Fig. 1 relates to pressureless-sintered MgO-doped commercial grade Si_3N_4 , Fig. 2 to gas-pressure-sintered Y_2O_3 -doped research grade Si_3N_4 . Porod, MSANS and volume-weighted mean pore diameters, and some mean grain diameters from SEM images, are marked in Fig. 1. At high density, grains coarsen while pores shrink slightly. Comparison of MSANS and Porod pore diameters (from SANS or USAXS Porod scattering) confirms that sintering is stable, pore size distributions neither narrowing nor broadening with densification. A change in pore size distribution, evident at 92% TD, is probably associated with microcracking as equiaxed alpha grains start to transform to elongated beta phase grains. Fig. 2 shows broad unimodal pore size distributions, with pore shrinkage apparent at high densities (grain coarsening similar to MgO-doped case). Complete absence of a separate fine pore population indicates a likely absence of microcracking during the phase transformation. MaxEnt volume fractions are less than true porosities, likely due to a reduced scattering contrast from the sintering aid, combined with glassy silica phases, lining the pore space (Porod diameters deduced from USAXS with corrections for contrast reductions). Differences in pore size evolution for the two cases are striking, illustrating how such studies can quantify differences in the statistically-representative microstructural evolution under varied processing conditions.

Figure 1. Volume-weighted porosity distributions in late-stage pressureless-sintering of MgO-doped silicon nitride.

Figure 2. Volume-weighted porosity distributions in late-stage pressureless-sintering of yttria-doped silicon nitride.

Diffraction Imaging of ZnSe Substrates for Blue/Green Emitters

X23A3

David Black, Harold Burdette (NIST), Gene Cantwell (Eagle-Picher Research Lab)

The unique capabilities of X23A3 have been used to study the defect microstructure of ZnSe single crystals grown by Eagle-Picher. We have observed defects such as subgrain boundaries, inclusions, inhomogeneous strain and residual subsurface damage. Surface reflection images show a texture which is related to the bulk defect density. Subsurface damage, observed from as polished crystals with nearly mirror smooth surfaces, results from the processing of these wafers from the as-grown boules. Highly asymmetric (grazing incidence) diffraction images improve our sensitivity to surface damage and these images have revealed an "orange peel" texture in the microstructure that probably results from chemo-mechanical polishing of the surface. The high quality of the crystals allowed us to obtain anomalous transmission images as shown below. The dislocation density calculated from selected areas is between 640 and 1300/cm².

Figure 1. A (220) symmetric transmission image taken with 9.5 keV x-rays.

Studies of Plasma-Sprayed Deposits using USAXS

X23A3

J. Ilavsky (SUNY at Stony Brook, NIST), G. G. Long, and A.J. Allen (NIST)

The structure of the porous phase in plasma-sprayed ceramic deposits made of alumina (3wt% titania) was studied using ultra-small-angle X-ray scattering (USAXS). The data were combined with small-angle neutron scattering measurements using overlapping scattering vector (Q) ranges, and achieving a scatterer size range from 20 Å to 2 μm (diameter).

The porous microstructure in plasma-sprayed deposits is mainly formed by two void systems - interlamellar pores and microcracks - each with different anisotropy. The microstructure has rotational symmetry around the spray direction but there is significant anisotropy in the two directions perpendicular to the spray direction.

The USAXS measurements yield slit-smeared data. To obtain separate information on the two void systems, measurements are made with different Q orientation with respect to the anisotropy.

Porod results showed that there are two scatterer populations: one with size larger than 2 μm (with surface area about $0.3 \times 10^4 \text{ cm}^2/\text{cm}^3$) and one with smaller scatterers (surface area around $2 \times 10^4 \text{ cm}^2/\text{cm}^3$). Further analysis requires shape assumptions on the smaller scatterers and is under further evaluation.

Figure 1. Modified Porod plot (IQ^4 vs Q^4 for measurements with Q oriented differently with respect to the substrate. The plateau at small Q suggests the presence of a second void system with large sizes (above about 2 μm).

Submicron Resolution Strain Mapping of an In-situ Strained High-Tc Superconductor Composite Tape by Microradiography

X23A3

R.D. Spal (NIST), G.N. Riley and C. Christopherson (American Superconductor Corp.)

Strained multifilamentary Bi-2223/Ag high-Tc superconductor composite tapes exhibit substantial critical current (I_c) at strains well past the critical strain at which I_c drops sharply from its unstrained value (Otto et al., IEEE Trans. Appl. Supercond. 3, 915, 1993). To study this behavior, the strain distribution in a tape tensilely strained in-situ to 0.91% was determined non-destructively by microradiography. Figure 1 shows pre- and post-strain images recorded digitally by an asymmetric Bragg diffraction microscope at 24.4 keV. The two bright vertical streaks in the post-strain image are strain-induced cracks in the filaments. Figure 2 shows the strain distribution along the filaments, determined by image analysis. Each point in the graph represents a 20 μm wide strip across the full image height; its abscissa is the strip's position in the pre-strain image, and its ordinate is the strip's horizontal displacement from pre- to post-strain images.

The magnitudes of the discontinuities are the opening dimensions of the cracks. The relatively small variation in displacement away from the discontinuities shows the strain is concentrated at the cracks.

Figure 1. Pre- (top) and post-strain (bottom) images; 1.25 x 0.20 mm² each.

Figure 2. Uniaxial strain distribution determined from fig. 1.

M. Endregard (Univ. of Trondheim, Norway), A. F. Gualtieri, S. Quartieri, G. Vezzalini (Univ. of Modena, Italy), and K.I. Pandya (NCSSU).

Zeolites are microporous crystalline solids with a framework structure composed of corner sharing TO_4 tetrahedra. Si or Al are the usual T elements which can be replaced partially by other elements such as Fe (generally in small percentages). XRF or EPM analyses of natural samples often show minor amounts of iron, but its nature is in many cases unclear and debated. Three major hypotheses have been advanced in literature: 1) Fe substitutes for Al in the framework, 2) Fe is present as an extra-framework cation, 3) Fe is structurally related to impurities such as hydroxides or oxides. It is experimentally difficult to elucidate the state of Fe because submicronic iron hydroxide and -oxide particles can not be separated from the zeolite material. If Fe is present as an exchangeable cation, low concentrations make it difficult to detect Fe in the exchanged solution. Furthermore, a sample can contain iron in all three possible sites. Mössbauer and XAS studies devoted to localizing Fe in zeolites have been successfully performed on synthetic samples [1], whereas, to the authors knowledge, not on Fe in natural samples. Local structural information about Fe derived from XAFS can provide some information on the state of Fe in zeolites. If Fe substitutes for Al, the zeolite lattice would require Fe to be tetrahedrally coordinated to 4 O. While Fe present as extra-framework cations or hydroxide/oxide impurity phases would most likely contain six-coordinated Fe. Three samples have been selected among a variety of natural zeolites: a mordenite [2], a ferrierite [3], and a heulandite [4] containing about 0.71, 3.29, and 1.55 % of $\text{Fe}_2\text{O}_3 + \text{FeO}$, respectively. We have collected RT Fe K-edge XAFS data in fluorescence mode on these samples and selected model compounds. Figure 1 shows the normalised XANES spectra of the zeolite samples. The intensity and position of the pre-edge peak has been used as a useful diagnostic feature of the coordination of Fe. [1] Preliminary analysis of our data is consistent with Fe in prevalent octahedral coordination.

[1] Bordiga S., Geobaldo F., Lamberti C., Zecchina A., Boscherini F., Genoni F., Leofanti G., Petrini G., Padovan M., Geremia S., and Vlaic G. (1995). Nucl. Instr. and Meth. in Phys. Res. B97, 23-27.

[2] Passaglia E. (1975). Contrib. Mineral. Petrol. 50, 65-77.

[3] Alietti A., Passaglia E., and Scaini G. (1967). Am. Min. 52, 1562-1563.

[4] Passaglia E. (1969). Per. Mineral. 2, 237-243.

Figure 1. Normalised Fe K edge spectra for the investigated natural zeolites.

A. Malik, W. Lin, M. K. Durbin, S. B. Roscoe, A. G. Richter, T. J. Marks and P. Dutta (Northwestern University)

We have used specular reflectivity to probe the microstructure of chromophoric self-assembled multilayers containing high β chromophores. These films were prepared by a repetition of a three step process consisting of depositing a coupling agent, the NLO active chromophore, and a capping agent. We have investigated the structural changes that take place due to subtle changes in the molecular building blocks. Films containing 1 to 10 layers were studied and the thickness increases linearly with number of layers in all cases. A plot of thickness versus number of layers, for the systems studied is shown in figure 1. Typical reflectivity data for these systems are shown in figure 2.

We first studied the effect of changing the anion in the coupling agent. Systems containing chlorine, bromine or iodine were compared. We find that the average layer thickness in films containing the chlorine and bromine coupling agents both agree well with molecular models (26.4 Å for the chlorine system, 25 Å for the bromine system). In contrast the average thickness increases to 36 Å when we switch to the iodine system.

We used the chlorine coupling agent to study the differences in films containing two different chromophores. Stilbazolium and azobenzene chromophores were compared. We find that films containing azobenzene chromophores tend to be thinner (23.2 Å per layer) than films with stilbazolium chromophores.

1) W. Lin, S. Yitzchaik, W. Lin, A. Malik, M. K. Durbin, A. G. Richter, G. K. Wong, P. Dutta and T. J. Marks, Angew. Chem. Int. Ed. Engl. 34, 1497 (1995).

2) S. B. Roscoe, A. A. Kakkar, T. J. Marks, A. Malik, M. K. Durbin, W. Lin, G. K. Wong and P. Dutta, Langmuir in press.

This work was supported by the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR9120521)

Figure 1. Thickness as a function of number of layers for the four systems.

Figure 2. Typical reflectivity data for multilayers (6 layers) of the systems studied.

Angular Correlation in Electron/X-ray Coincidence Spectroscopy

X24A

U. Arp (NIST), T. LeBrun, S. Southworth, M. Jung (ANL), and J. Cooper (UMD)

Last year we reported a new coincidence technique to select a certain decay pathway in the deexcitation cascade of an atom after deep inner-shell photoionization/excitation. The resulting spectra could be explained using Hartree-Fock calculations [1,2]. Certain intensity changes in coincident recorded electron spectra compared to normal electron spectra motivated a theoretical study on angular correlation effects [3] in the coincidence spectra. When two particles are detected coincident with some angular resolution, angular correlation will affect the spectra. In this case the propagation direction of the detected fluorescence photon defines the quantization axis for the angular distribution in the following Auger-process. In the theoretical analysis of the experiment we found intensity changes depending on the direction in which the photon is detected. Knowing this we initiated an experiment aimed at these effects and first preliminary results using a large area avalanche photo diode showed agreement with theory.

- [1] T. LeBrun et al., in preparation for Phys. Rev. Lett.
- [2] U. Arp et al., in preparation for Phys. Rev. A.
- [3] N. Kabachnik et al. J. Phys. B: At. Mol. Opt. Phys. 24, 2249 (1991).

Resonant x-ray fluorescence study of uranium oxides

X24A

S. M. Butorin, J. Nordgren (Uppsala U., Sweden), Y. Ma (U. of Washington and Pacific Northwest Labs.), K. E. Miyano (Brooklyn College), D. C. Mancini (U. of Lund, Sweden), B. A. Karlin (NIST), and D. K. Shuh (LBL)

The U 5f-to-3d x-ray fluorescence spectra of UO_2 and UO_3 were recorded at different excitation energies near the U 3d threshold. For UO_2 , the resonant part of the fluorescence (Fig.1) consists of the "recombination" line and a broad structure at lower energies which can be attributed to the core-hole decay to the states of $5f^2$ and $5f^3v$ (v stands for a hole in the valence band) configurations, respectively. This shape of the resonant spectra is due to the configuration mixing in the ground and intermediate states of the x-ray fluorescence process as a result of the transfer of an electron from the valence band to the 5f level. For UO_3 , the triple-line shape of the U 5f-to-3d fluorescence spectrum (Fig.2) excited with 3563.9-eV photons indicates that the ground state of UO_3 is a mixture of $5f^0$, $5f^1v$ and $5f^2v^2$ configurations. Tuning the excitation energies to satellites in the U M_5 absorption edge of UO_3 at about 3 eV and 10 eV above the main absorption maximum leads to an enhancement in the transition rate to $5f^1v$ and $5f^2v^2$ states in fluorescence spectra at about 8.5 eV and 14.5 eV below the recombination peak, respectively. These resonances indicate the charge-transfer origin of absorption satellites.

Figure 1. The U M_5 x-ray absorption and resonant U 5f-to-3d x-ray fluorescence spectra of UO_2 . The arrows indicate the excitation energies used for the fluorescence spectra.

Figure 2. The U M_5 x-ray absorption and resonant U 5f-to-3d x-ray fluorescence spectra of UO_3 . The arrows indicate the excitation energies used for the fluorescence spectra.

D. Heskett (URI), L.E. Berman, and C.-C. Kao (NSLS)

The (1x2) missing row reconstructions of FCC (110) metal surfaces induced by alkali adsorption have served as prototypic systems for the study of adatom-induced surface reconstructions. We have carried out the first investigation of such a system using the technique of x-ray standing waves (XSW). Our XSW investigation of the system Rb/Cu(110) was carried out on beamline X24A in the back-reflection configuration with measurements in the (220) and (111) geometries. Auger and photoelectrons were collected with a single-pass CMA. In Figure 1 we present a typical data set from our (111) measurements of the Rb $2p_{3/2}$ core level. Our most significant result is the relatively high coherent fraction we observed for the rubidium atoms in this geometry ($\sim 0.5-0.8$), indicating a relatively high degree of order parallel to the surface along the [01] direction, which is across the missing rows. This result is quite different from our previous study of Rb/Cu(111) (1,2), for which we observed very low coherent fractions (< 0.2) for all coverages in the geometry parallel to the surface. For Rb/Cu(110) we account for our results by assuming that the missing row nature of the reconstruction "locks" the Rb atoms into the missing row troughs. In a recently completed XSW study which probed the order in the [10] direction along the rows, we found the degree of order to be significantly reduced, as indicated by a very low coherent fraction for this case, and which is consistent with our other results.

1. X. Shi, C. Su, D. Heskett, L. Berman, C.-C. Kao, and M. Bedzyk, Phys. Rev. B49, 14638 (1994).

2. D. Heskett, P. Xu, L. Berman, C.-C. Kao, and M. Bedzyk, Surface Science, in press.

Figure 1. The x-ray standing wave yield for the Rb $2p_{3/2}$ core level for (1x2)Rb/Cu(110) taken in the (111) reflection centered around an incident photon energy of 2974 eV. The upper curves are the XSW yield (dots) and simulation using dynamical diffraction theory (solid line). The lower curves are x-ray reflectivity (crosses) and fit (solid line).

Terrence Jach (NIST), S. M. Thurgate (Murdoch U.), Y. Zhang, R. Colella (Purdue U.), S. W. Kycia (Cornell U.), and A. I. Goldman (Iowa State U.)

X-ray diffraction from very perfect quasicrystal specimens might be expected to demonstrate the nature of dynamical diffraction in the quasilattice. The Darwin width of the rocking curve is due to a "structure factor" which does not originate from a periodic unit cell. The meaning of the α and β branches of the dispersion surface is less clear than for atoms occupying periodic positions relative to the diffraction planes in a normal crystal.

We have observed diffraction from the (420024) and (640046) reflections of an AlPdMn quasicrystal in the back-reflection Bragg geometry ($\theta_B = 90^\circ$). The rocking curves observed by scanning the X24A monochromator in energy display Darwin widths consistent with dynamical theory (Fig.1). X-ray $K\alpha$ fluorescence observed from the Al atoms during the scan exhibits x-ray standing wave behavior similar to that of a crystalline material (Fig. 2). The data suggest a "coherent position" for the Al atoms and the first direct observation of long range ordering of specific elements in the quasicrystal.

Figure 1.

Figure 2.

Non-dipolar asymmetries of photoelectron angular distributions

X24A

M. Jung, B. Krässig, D.S. Gemmell, E.P. Kanter, T. LeBrun, S.H. Southworth, and L. Young (Argonne National Laboratory)

We have measured the non-dipolar contributions to the Ar 1s, Kr 2s, and Kr 2p photoelectron angular distributions using 2 - 5 keV polarized x-rays from beamline X24A. The non-dipolar interaction results in a forward/backward asymmetry with respect to the photon beam. This asymmetry was measured by rotating an electron spectrometer about the polarization vector with a fixed polar angle of 54.7° , thus eliminating the angular dependence on the β parameter. Figure 1 shows the setup used in the experiment. The CMA was used for normalisation. We rotated the parallel plate analyser (PPA) several times in steps of 15° with a dwell time of typically 1 minute and a total time of 5 minutes per point.

Figure 2 shows our measured values of the non-dipolar asymmetry parameter γ for Kr 2s in comparison with Cooper's calculations [1], which include interference between the electric-dipole and electric-quadrupole photoionization amplitudes. The Kr 2s asymmetry is directed forward near threshold, is slightly backward directed for electron energies between 900 eV and 2300 eV, and becomes increasingly forward directed at higher energies. The γ parameter for Ar 1s and Kr 2p shows a very different energy dependence but is also in good agreement with Cooper's [1] and Bechler and Pratt's [2] calculation. You can find further details in [3]. [1] J.W. Cooper, Phys. Rev. A 47, 1841 (1993)

[2] A. Bechler and R.H. Pratt, Phys. Rev. A 39, 1774 (1989); 42, 6400 (1990)

[3] B. Kraessig et. al., Phys. Rev. Let. 75, 4736 (1995)

Figure 1. Experimental setup with coordinates used for the description of photoelectron angular distributions.

Figure 2. Asymmetry parameter γ in dependence on electron kinetic energy for Kr 2s compared with Coopers theoretical values.

X-ray scattering of atoms and molecules

X24A

K. Miyano (CUNY), U. Arp (NIST), and S. Southworth (ANL)

The diagram K beta fluorescence spectrum of OCS after 1s photoionization of sulphur [1] has been known for many years. A recent calculation by Meehan et al. [2] predicted a strong influence of the spectator electron in the resonant scattering case, which initiated this experiment in which we looked in the fluorescence after resonant excitation or the resonant inelastic scattering using a bend crystal spectrometer.

The resonance fluorescence appears different from the diagram fluorescence opening a rich source of information on molecular structure, even more so if a polarization analysis is performed, which gives directly information on the symmetry of the involved molecular states. In a second experiment we were looking for the Compton-scattering of atomic argon at 2982 eV and 4000 eV incident photon energies. We found very broad peaks at energies lower compared to the Rayleigh-scattered peaks, but these peaks are shifted by the same energy at both energies, which makes clear that this is no Compton-scattering. Much more likely is a scattering process where a valence electron is photoionized and then recombines to a highly excited state [3].

[1] R.C.C. Perera and R.E. LaVilla, J. Chem. Phys. 81, 3375 (1984).

[2] T.E. Meehan, T.R. Walsh and F.P. Larkins, to be published.

[3] V.B. Berestetskii, E.M. Lifshitz and L.P. Pitaevskii, Quantum Electrodynamics (Pergamon, Oxford, 1982).

An electron-electron coincidence experiment near the Ar K-edge * X24A

R. Wehlitz, L. Pibida, J.C. Levin, and I.A. Sellin (Univ. of Tenn.)

During our first beam time of this project we have taken electron spectra as well as electron-electron coincidence spectra around the Ar K-edge. The monochromatized synchrotron light was intersecting an effusive gas beam. Electrons coming from this interaction region were detected with a cylindrical mirror analyzer (CMA) and a time-of-flight (TOF) spectrometer. The TOF spectrometer was mounted horizontal and the CMA was mounted vertical in a plane perpendicular to the photon beam. The CMA was equipped with a position sensitive anode, thereby capable of measuring the angular distribution of electrons. In order to detect electrons of low kinetic energies, the chamber was covered with μ -metal on the inside. The electron spectra taken on the Ar $1s \rightarrow 4p$ resonance reveal a complex structure of low kinetic energy Auger lines (particularly around 5eV) not seen before (Fig. 1). However, the intensity is too low for a detailed analysis of these Auger lines yet, but will be part of future investigations. The main goal of our investigations was to record the Ar LMM Auger lines in coincidence with one KLL Auger line to disentangle the complex structure of the LMM Auger group. While the CMA was tuned to the KL_2L_3 Auger line, the group of LMM Auger lines was detected with the TOF spectrometer (Fig. 2). Unfortunately the line width was broader than expected due to our electronics. Modifications for our next beam time are expected to increase the time resolution and will enable us to analyze the line structure of the LMM Auger lines.

Figure 1. Low energy part of a TOF Auger electron spectrum taken on the Ar $1s \rightarrow 4p$ resonance

Figure 2. LMM Auger lines in coincidence with the KL_2L_3 Auger line on the Ar $1s \rightarrow 4p$ resonance

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Strain relaxation of ultrathin InAs/GaAs(001) films

X24A

J.C. Woicik (NIST), K.E. Miyano (Brooklyn), J.G. Pelligrino (NIST), P.S. Shaw (NIST), S.H. Southworth (NIST), and B.A. Karlin (BNL)

The strain relaxation of ultrathin InAs films embedded in host GaAs(001) has been followed by the x-ray standing wave and extended x-ray absorption fine-structure techniques. While 1 monolayer (ML) films are found to be tetragonally distorted in accordance with the prediction of macroscopic-elastic theory, thicker films are found to collapse to their natural-lattice constant past a critical thickness, T_c , of 2 ML. By 8 ML, bond-length strain is no longer evident, and a large degree of structural disorder is observed.

Refractive and extinction indices of Lithium Triborate in 55-71 eV region *	X24C
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T.J.Chen (Southern Illinois U.), W.R.Hunter (Sachs Freeman Assoc.), R.Zitter, R.Tao (Southern Illinois U.), J.C.Rife (NRL)

Nonlinear optical crystal lithium triborate (LiB_3O_5 , or LBO) has direct band gap at ~ 7.8 eV, therefore it is opaque in 55-71 eV region. The refractive indices n_j ($j=x,y,z$), and extinction indices k_j ($j=x,y,z$) for three principal polarizations were derived from the measured reflection spectra in 55-71 eV region. In the derivation, the electric dipolar oscillator model was used: assuming $n_j(E)$ and $k_j(E)$ can be obtained by the complex refractive indices $\tilde{n}=n+ik$, and it can be found by Snell's law:

$$\sin\theta = \tilde{n}_j \sin\tilde{\theta}_j$$

And the complex refractive index $\tilde{n}$ is related to the complex dielectric constant $\tilde{\epsilon}_j$

$$\tilde{\epsilon}_j = \tilde{n}_j^2 = 1 + 4\pi\chi_j = 1 + \sum_i \left[\frac{M_{ij}(E_{ij} - E)}{(E_{ij} - E)^2 + \Gamma_{ij}^2} + \frac{M_{ij}\Gamma_{ij}}{(E_{ij} - E)^2 + \Gamma_{ij}^2} \right]$$

where the summation goes over $i=1,2,3,4,5,b,r$; the oscillators of 1-5 represent the transitions observed in our experiments. All other oscillators outside our spectral region are represented by two terms: the b for higher energy side, and r for lower energy side. Then the Fresnel formula was used to calculate the reflectance to fit the experimental data. The following parameters were obtained from the best fit and are listed in the table:

	x			y			z		
	$E_i(\text{eV})$	M_i	$\Gamma_i(\text{eV})$	$E_i(\text{eV})$	M_i	$\Gamma_i(\text{eV})$	$E_i(\text{eV})$	M_i	$\Gamma_i(\text{eV})$
1	60.00	.032	.70	59.9	.033	.30	59.8	.005	.28
2	61.50	.031	.95	61.2	.036	.85	60.9	.059	1.6
3	62.6	.018	.90	—	0	—	62.9	.051	1.6
4	65.5	.006	.80	64.3	.004	.60	65.5	.021	1.2
5	67.8	.042	2.5	67.4	.080	2.8	67.9	.057	2.2
r	29.0	9.56	15.8	41.5	5.7	15.2	47.9	3.46	8.8
b	86.0	2.80	6.0	86.0	2.20	6.0	86.0	0.80	6.00

Figure 1.

* This work is supported by Illinois Board of Higher Education.

Photoemission and C-1s near-edge absorption from photopolymerized C_{60} films *	X24C
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B.S. Itchkawitz (Fritz-Haber-Institut, Berlin), J.P. Long (NRL), T. Schedel-Niedrig (Fritz-Haber-Institut, Berlin), M.N. Kabler (NRL), A.M. Bradshaw, R. Schlogl (Fritz-Haber-Institut, Berlin), W.R. Hunter (SFA, Inc.)

Photopolymerization of pure C_{60} films has been characterized using valence-band and C-1s photoemission and near-edge absorption spectroscopy [1]. Figure 1 compares valence-band PES of pristine films with those of films polymerized to saturation at 300K by pulsed radiation from a Cu vapor laser (2.43 eV, 5 ns). Data for four synchrotron-radiation energies are shown, along with calculated (LDA) densities of states for C_{60} molecules (solid curve) and polymerized dimers[2]. Similarities between measured and calculated features are evident. The C-1s data suggest that roughly 12% of all C atoms is engaged in new bonding. The photopolymerization efficiency at 84K is less than 1% of that at 300K. Kinetics at three fluences are illustrated in Fig. 2, which shows the rise with dose of a simple saturating function of the amplitude A of spectral features associated with polymerization. The rate constant, shown vs. peak laser intensity in the inset, becomes sublinear at high intensity. This suggests concentration dependent recombination of those excited states which are precursors to polymerization. The line in the inset is an extrapolation of prior Raman data [3] for laser intensities lower by a factor 10^5 than used here.

- [1] B.S. Itchkawitz et al., *Chem. Phys. Lett.* 243, 211 (1995).
- [2] M.R. Pederson and A.A. Quong, *Phys. Rev. Lett.* 74, 2319 (1995).
- [3] Y. Wang et al., *Chem. Phys. Lett.* 211, 341 (1993).

Figure 1.

Figure 2.

* Supported in part by the German Federal Ministry of Science and Technology

Structural Determination of the $\beta\text{SiC}(100)\text{-c}(2\times 2)$ Surface from C-1s Surface-Core-Exciton and Si-2p Absorption * X24C

J. P. Long (NRL), V. M. Bermudez (NRL), D. E. Ramaker (George Washington Univ.)

The C-terminated (100) surface of βSiC , which reconstructs as $\text{c}(2\times 2)$, is important for its chemical inertness and thermal stability. Two structures, the π and σ models sketched in the figure, have been proposed for this surface. We have measured the polarization dependences of the near-edge absorption spectra of two C-1s surface core excitons (SCE). A sample of data is shown in the figure. Thresholds are marked, and insets show angle dependences. These data establish conclusively that the π structure, with staggered rows of π -bonded C dimers bridging underlayer Si dimers, is correct. This conclusion is supported both by Si L-edge NEXAFS, which provide evidence for Si dangling-bond states present only in the π -bonded model, and by MO cluster calculations, which identify these Si states and which support our interpretation of the polarization data. This work also verifies recent ab-initio calculations. Furthermore, we observe a strong resonant photoemission in the valence band which accompanies the de-excitation of the C-1s SCE. C dimers on $\text{SiC}(100)\text{-c}(2\times 2)$ are isolated and thus produce relatively strong SCE absorption features, unlike the extended states on diamond (111)-(2 $\times$ 1).

Figure 1.

Figure 2.

Characterization of Soft X-Ray Multilayer Gratings and Mirrors X24C

J. F. Seely, M. P. Kowalski, J. C. Rife, R. G. Cruddace (NRL), T. W. Barbee, Jr. (LLNL), and W. R. Hunter (SFA Inc.)

Multilayer-coated diffraction gratings and mirrors have been characterized in the soft x-ray region using the monochromator and reflectometer at beamline X24C.

The multilayer coatings (e.g. Mo/Si and W/B₄C) are sputter deposited and are designed to have high reflectance at the energies and angles of incidence of interest for astrophysical, solar, and laboratory applications. The grating substrates are produced by the holographic ion-etched process or are replicas of ruled master gratings. The mirror substrates are flats or spherical and are super-polished. The reflectance of the multilayer mirrors and the efficiency of the multilayer gratings are measured in the energy range 10-1000 eV and at angles ranging from near normal to grazing.

* This work was supported in part by the Office of Naval Research

X-Ray Standing Wave Investigation of c(4x2) CO/Ni(111)

X25

L.E. Berman (NSLS), D.R. Heskett (U. Rhode Island), and C.-C. Kao (NSLS)

Measurements of the site preferences of the C and O constituents of the diatomic molecule CO, adsorbed on a Ni(111) substrate surface, were undertaken using the x-ray standing wave technique. A clean Ni(111) substrate surface was dosed, below room temperature, with one-half monolayer of CO, forming a c(4x2) overlayer geometry. The yields of the Ni 2p_{3/2}, O 1s, and C 1s core levels were measured separately, using a cylindrical mirror analyzer, as the bulk Ni(111) and Ni(11 $\bar{1}$) Bragg reflections were scanned, and were compared with theory to determine the positions of these atom constituents relative to the respective Bragg planes. An energy distribution curve, measured by scanning the analyzer, is shown in Figure 1, and x-ray standing wave (XSW) data for Ni, O, and C are shown in Figure 2 for the (111) reflection. Assuming the CO molecular axis to be oriented perpendicular to the (111) surface, the (111) reflection data yield directly a C-O bond length of 1.10 ± 0.06 Å, in good agreement with theoretical calculations. A model in which the CO molecules adsorb in a 50-50 mixture of 3-fold fcc and hcp hollow sites, with the C atom closer to the substrate and elevated by 1.40 ± 0.04 Å above the topmost bulk-like Ni atom plane, accompanied by some disorder, compares favorably with the observed results using the (111) and (11 $\bar{1}$) Bragg reflections. This is consistent with the results of recent SEXAFS and PED measurements of this system, and inconsistent with a 2-fold bridge site assignment based on earlier infrared and EELS studies of this system.

Figure 1. Electron energy distribution curve of CO/Ni(111) measured at a photon energy of 3.055 keV.

Figure 2. Measured XSW yields of the Ni2p_{3/2}, O 1s, and C 1s core levels as the bulk Ni(111) Bragg reflection (at bottom) was scanned, compared with theoretical fits, for c(4x2) CO/Ni(111).

Real-Time Small-Angle X-ray Scattering Studies of Rubber-Modified Engineering Thermoplastics

X25

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Real-time small-angle X-ray scattering (RTSAXS) studies were performed on a series of rubber-modified thermoplastics. These include rubber-toughened syndiotactic polystyrene (sPS), High Impact Polystyrene (HIPS), and Acrylonitrile Butadiene Styrene-type copolymers (ABS). The data from the rubber-toughened sPS is of interest because the specific gravity of the crystalline and amorphous phases are nearly identical, thus permitting the study by RTSAXS of a toughened semi-crystalline polymer without undue SAXS interference from scattering from the crystalline lamellar microstructure. Linear small-angle X-ray scattering patterns were measured at successive time intervals as short as 3 ms. using a Reticon detector coupled to an optical multichannel analyser. The patterns were analyzed to determine the plastic strain due to crazing. Simultaneous measurements of the absorption of the primary beam by the sample using a semi-transparent beam stop fitted with a pin diode allowed the total plastic strain to be computed. The plastic strain due to other deformation mechanisms (e.g. particle cavitation and macroscopic shear deformation) was determined by the difference. The contribution from microscopic shear deformation was determined from video-based optical data obtained along with the RTSAXS data. The run was very productive in data with the equivalent of over 200,000 linear SAXS patterns being generated. Activity is now focused on developing and using software to rapidly analyse this great quantity of data, while in the interim data from key samples are analysed individually.

Using this technique, samples of commercial thicknesses can be studied at high rates of deformation without the inherent limitations of microscopy and its requirement of thin samples (i.e., plane strain constraint is maintained on sample morphology). Contrary to the conclusions drawn from many previous dilatation-based studies, it has been demonstrated that the strain due to noncrazing mechanisms, such as rubber particle cavitation, and deformation of the glassy ligaments between rubber particles, is more significant than the contribution due to crazing. One example of how the contribution from each mechanism of deformation can be delineated is with a comparison of acrylonitrile ethylene styrene (AES) and acrylonitrile styrene acrylate (ASA) systems in an SAN matrix. Manipulating the graft and crosslinking levels in the AES system results in a ten-fold increase in microshear yield, but not much additional crazing. Presumably, this is the result of better grafting of the rubber particles to the matrix and, thereby, inducing a balanced triaxial dilation force on the particles rather than having the particles prematurely detach from the matrix. Manipulating the ASA particle size in an AES/ASA blend resins resulted in about a 50% microshear and rubber particle cavitation, and a doubling the contribution due to crazing at fracture. These results are consistent with the mechanical testing of the samples wherein the AES/ASA blend was found to have greater impact strength than the straight AES system.

W.A.Caliebe, C.-C.Kao, L.E.Berman, J.B.Hastings (NSLS), M.H. Krisch, F. Sette (ESRF, France), K.Hämäläinen (University of Helsinki, Finland)

In the last 20 years many different techniques have been developed in order to study the spin resolved electronic structure of many metals. We combined one of these techniques, X-Ray Magnetic Circular Dichroism (XMCD), with X-Ray Resonant Raman Scattering in order to study the L_{III} -edge of Gd. We excited the intermediate states $2p^5 4f^7 5d^1$ (quadrupolar transition) and $2p^5 4f^{7+1} 5d^0$ (dipolar transition) with circular polarized X-rays and observed with high energy resolution the fluorescence emitted during the decay into the final states $3d^9 4f^7 5d^1$ and $3d^9 4f^{7+1} 5d^0$ respectively. The final data, including corrections for the degree of polarization, angle between the magnetic field and the photon beam, and the magnetization are shown in figure 1. The relatively weak quadrupolar transition is clearly separated from the strong dipolar one, which is split into two peaks with different electron spin.

This techniques allows to obtain information about the L_{III} -edge in Gd but we also obtain indirectly information about the $M_{IV,V}$ -edge, because the final state is the same. A more detailed analysis is in progress.

Figure 1. Spin resolved resonant raman spectra of Gd. The two curves represent the intensity for parallel and antiparallel electron and photon spin.

* Supported by US DOE under contract # DE-AC02-76CH00016.

Kelly A. Daly (University of Michigan), Melissa M. Grush (University of California-Davis) and James E. Penner-Hahn (University of Michigan)

X-Ray spectroscopy has been used in the past as a tool in determining transition metal electronic structure and coordination environment. Many limitations arise in analyzing amorphous, solution and dilute samples such as powders and proteins. Using a high-resolution x-ray emission monochromator to select emission energy, emission intensity was collected as a function of excitation energy and emission energy. The added resolution of the emission monochromator and the expansion of data collection into a second dimension allowed us to separate the individual electronic transitions on the K edge. Data were collected on a tetranuclear manganese compound, $[Mn(IV)_4O_6(1,4,7\text{-triazacyclononane})_4](ClO_4)_4$. Each manganese exists in a pseudo-octahedral environment with three oxygen at 1.80 Å and three nitrogen at 2.08 Å. Data were collected in the $K\beta$ emission region ($3p \rightarrow 1s$ transition) and in the excitation regions corresponding to the $1s \rightarrow 3d$ transition, the $1s \rightarrow 4p$ and other edge transitions and continuum transitions past the edge threshold. The figure shows the $K\beta$ emission spectra collected at various excitation energies in the $1s \rightarrow 3d$ region. In pseudo-octahedral manganese(IV), there are two expected $1s \rightarrow 3d$ transitions; to the e_g and t_{2g} orbitals. The shape and peak maxima change as the excitation energy is advanced showing the majority of the states exist initially with the excited electron in the t_{2g} orbitals, but as the excitation energy is increased, the higher energy orbitals, e_g , become populated to a higher percentage with the excited electron causing an increase in emission energy. An increase of 4 eV in excitation energy resulted in an increase of 1.3 eV in emission energy. Emission data collected on and past the edge show enhancement of the $1s \rightarrow 4p$ transition on the edge. These data exhibit the same behavior as the data collected in the $1s \rightarrow 3d$ region, with an increase in emission maxima by 0.3 eV as the excitation energy is increased by 5 eV. Once the continuum is reached, the emission maximum drops 0.7 eV in energy.

Figure 1.

* With thanks to Prof. Stephen Cramer for the use of equipment and to Prof. William H. Armstrong for the manganese compound. Funded in part by NIH grant GM-45205.

The crystal structure of a hyperthermophilic Archaea TATA binding protein	X25
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B. S. DeDecker*, R. O'Brien†, P. J. Fleming*, S. P. Jackson‡ & P. B. Sigler*
 (*Howard Hughes Medical Institute and Yale University; †Yale University; ‡Wellcome/CRC Institute and Cambridge University)

Hyperthermophilic organisms have an optimal growth temp. above 80°C and are able to grow at temp. exceeding 90°C (1). Based on phylogenetic studies most hyperthermophilic genera have been classified as Archaea, while two are Bacteria (2). It has been proposed that the common ancestor of all existent life was a hyperthermophile, and that relatively modern mesophilic biology is an adaptation from an earlier hot environment (3). The organism *Pyrococcus woesei* is a hyperthermophilic Archaea found near deep-sea hydrothermal vents with an optimal growth temp. of 105°C. In concurrence with the observation that the Archaea cell and the eukaryotic nucleus share a common ancestor, homologues of the eukaryotic transcription factor TATA binding protein (TBP) have recently been cloned from *P. woesei* and other Archaea species (4, 5). The crystal structures of two eukaryotic TBPs are known, one from the plant species *Arabidopsis thaliana* at 2.1 Å resolution and the other from the yeast *Saccharomyces cerevisiae* at 2.6 Å resolution (6, 7). Here we report the structure of the Archaea TBP from *P. woesei* at 2.2 Å resolution, with the native data set for this study having been collected at the NSLS X25 beamline.

At room temp., *P. woesei* TBP binds DNA with an affinity a 1,000 fold lower than its eukaryotic homologues. This characteristic, as shown by the crystal structure, is due in part to the dramatically different electrostatic surface of Archaea TBP. In addition, the *P. woesei* TBP structure demonstrates a correlation between protein packing and hyperthermostability. This hyperthermophilic protein is currently the most efficiently packed of all reported structures in the PDB; exceeding the previous theoretical limit of protein core packing density which is that found in crystalline hexane (8). This structure offers a window into the evolution of eukaryotic transcription and the structural basis of thermostability.

[1] M. W. W. Adams. (1993) Enzymes and proteins from organisms that grow near and above 100°C. Annu. Rev. Microbiol. 47: 627-658.

[2] C. R. Woese, O. Kandler, M. L. Wheelis. (1990) Towards a natural system of organisms: Proposal for the domains Archae, Bacteria, and Eucarya. Proceedings of the National Academy of Sciences, USA 87: 4576-4579.

[3] C. R. Woese. (1987) Bacterial Evolution. Microbiological Reviews: 221-271.

[4] T. Rowlands, P. Baumann, S. P. Jackson. (1994) The TATA-Binding Protein: A Genl. Transcription Factor in Eukaryotes and Archaeobact. Sci. 264: 1326-1329.

[5] T. L. Marsh, C. I. Reich, R. B. Whitelock, G. J. Olsen. (1994) Transcription factor IID in the Archae: Sequences in the *Thermococcus celer* genome would encode a product closely related to the TATA-binding protein of eukaryotes. Proc. Natl. Acad. Sci. USA 91: 4180-4184.

[6] D. B. Nikolov, et al. (1992) Crystal structure of TFIID TATA-box binding protein. Nature 360: 40-46.

[7] D. I. Chasman, K. M. Flaherty, P. A. Sharp, R. D. Kornberg. (1993) Crystal structure of yeast TATA-binding protein and model for interaction with DNA. Proc. Natl. Acad. Sci. USA 90: 8174-8178.

[8] F. M. Richards. (1974) The Interpretation of Protein Structures: Total Volume, Group Volume Distributions and Packing Density. J. of Mol. Bio. 82: 1-14.

Near-edge studies of the Excitation of the K α satellites in copper *	X25
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M. Deutsch, O. Gang (Bar-Ilan U., Israel), K. Hämäläinen (Helsinki U., Finland.), C.C. Kao (BNL)

We measured the photoexcited lineshape of the K α satellite spectrum of Cu, for excitation energies from below to above the KL edge (9800-11200 eV). In contrast to the expectations of an abrupt edge structures in the fluorescent spectrum, corresponding to different L-spectator transitions, a smooth increase of the intensity was found. This points to a pure shake-off origin for the excitation process. The evolution of the lineshape and intensity from its appearance (10050 eV) up to its saturation (11200 eV) was studied. By fine tuning the excitation energy near threshold we found an energy difference of ~20 eV in the opening of the two channels (α'_4, α_4 and α_3, α'_3) which originate in 2p spectator transitions with different total momenta. Below this critical excitation energy (10050 eV) the satellites vanish. The opening energy of the channels agrees with the Z+1 approximation and our relativistic Dirac-Fock calculations, which also show a reasonable agreement with the lineshape measured. Analysis reveals that the shape of the satellite is basically unchanged from slightly above the threshold (~10050 eV) up to the highest excitation energy measured (11200 eV). Only the intensity of the complex grows.

Calculations in the adiabatic and transition-to-sudden approximation are required to elucidate this point.

Figure 1. Measured K α satellite spectrum of copper for the incident energies listed.

Figure 2. Intensity variation of the four satellite components with increasing incident energy.

* Supported by the German-Israel Science Foundation, Jerusalem.

Structure of the high affinity complex of an inositol trisphosphate with a phospholipase C pleckstrin homology domain.	X25
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K.M.Ferguson(Yale), M.A.Lemmon, J.Schlessinger(NYU) and P.B.Sigler(H.H.M.I, Yale)

PH domains have been identified on the basis of primary sequence similarity of an approximately 100 amino acid motif found in many proteins involved in signaling processes. In phospholipase C- δ (PLC- δ) this domain is located towards the N-terminus of the protein in a region responsible for high affinity inositol trisphosphate and phosphatidyl inositol biphosphate binding. We have solved the X-ray crystal structure of the high-affinity (210 nM, [1]) complex between the pleckstrin homology (PH) domain from rat PLC- δ_1 and inositol-(1,4,5)-trisphosphate (Ins(1,4,5)P₃). The structure was solved by multiple isomorphous replacement plus anomalous scattering using phase information from a data set collected at X-25 on crystals grown from seleno-methionine protein, plus data from a mercury derivative collected on a home source. The structure has been refined to 1.9 Å resolution against the data collected at X-25, to a final R-value of 20.5 % ($\geq 2 \sigma$ data). The fold of the PLC- δ_1 PH domain is similar to others of known structure. Ins(1,4,5)P₃ binds in the center of the positively charged face of the electrostatically polarized domain, making extensive interactions with the $\beta 1/\beta 2$ and $\beta 3/\beta 4$ loops of the PH domain. The 4- and 5-phosphate groups of Ins(1,4,5)P₃ interact extensively, while the 1-phosphate participates in one hydrogen bond. Two amino acids in PLC- δ_1 PH that contact Ins(1,4,5)P₃ have counterparts in the Bruton's tyrosine kinase (Btk) PH domain where mutational changes cause inherited agammaglobulinemia, suggesting a mechanism for the loss of function in Btk mutants. Using electrostatics and varying levels of head-group specificity, PH domains may localize and orient signaling proteins providing a general membrane targeting and regulatory function.

[1] Lemmon,M.A., Ferguson,K.M., Sigler,P.B. and Schlessinger,J. (1995) Proc. Natl. Acad. Sci. (USA), in press.[2] Ferguson,K.M., Lemmon,M.A., Schlessinger, J. and Sigler,P.B. (1995) Cell, in press.

Structural Studies of the Human Transferrin Receptor and a bZIP protein/DNA complex. *	X25
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S.C. Harrison and C.M. Lawrence (HHMI, HU, Children's Hospital)

Human transferrin receptor (TfR): We made significant progress in this very challenging structure determination.

Data were collected from crystals of SeMet substituted TfR. There are too many methionine residues for this to be a first isomorphous derivative, and the unit cell is too large for this to be a good candidate for MAD experiments, but the data will be important for phasing, once a first conventional derivative is obtained, and for tracing a polypeptide chain. The SeMet data set is 70% complete to 6 Å; the R_{merge} for all data is 0.095. We also collected additional native data, which merged well with data (to 3.2 Å) collected previously at CHESS.

A bZIP protein/DNA complex: A data set, complete to 2.8 Å ($R_{merge} = 0.060$) was collected from crystals of a multiple mutant of GCN4, bound to a C/EBP DNA site. The goal of the structure determination is to understand bZIP specificity, since the mutated residues change the specificity to that of CE/BP, despite the fact that all but one are a non-contacting positions. The structure has now been determined by molecular replacement using these data, and refinement is in progress.

* This work was supported by the Howard Hughes Medical Institute

The 2.0 Å Crystal Structure of a Heterotrimeric G Protein

X25

David Lambright (Damon Runyon-Walter Winchell Fellow, Yale University) and Paul Sigler (Howard Hughes Medical Institute, Yale University)

Heterotrimeric guanine nucleotide binding proteins (G proteins; subunits α , β , and γ) couple agonist stimulated heptahelical receptors, located at the cell surface, to a variety of intracellular signaling pathways. We have recently completed the 2.0 Å crystal structure of the heterotrimeric (GDP bound) form of transducin, the heterotrimeric G protein that couples the light activated photoreceptor rhodopsin to the visual signaling cascade in retinal rod cells. The structure was solved at 3.0 by multiple isomorphous replacement using isomorphous differences from a $\text{Hg}(\text{OAc})_2$ derivative and isomorphous as well as single wavelength anomalous differences from a CH_3HgCl derivative and a selenomethionine (Se-Met) derivative substituted in the α subunit. In order to maximize the Bijvoet differences for the Se-Met derivative, intensities were collected at the peak of the Se absorption edge using the X25 beamline of the NSLS at Brookhaven. The Se-Met derivative was essential for obtaining initial phases. The initial MIR map was improved with solvent flattening and histogram matching.

The model has been refined with simulated annealing against the Se-Met intensities from 6.0 to 2.0 resolution. The present model has an R-value of 23.5 % for all data (22.0 % for data $> 2 \sigma$) and a free R-value of 30.6 % (29.2 % for data $> 2 \sigma$) for a randomly selected subset (10 %) of the data omitted prior to the start of refinement. A manuscript describing this work is in preparation.

Ratio of Double-to-Single Photo- and Compton Ionization of Helium

X25

Jon C. Levin, G. Bradley Armen, and Ivan A. Sellin (U. Tennessee)

Theoretical prediction of the energy dependence of the double ionization of helium by a single photon is a fundamental problem in atomic physics which requires solution of the Coulomb three-body problem. In the independent-particle framework, in which the photon can interact directly with only one electron, double ionization by a single photon can proceed only by electron-electron correlation. As a result, photoionization of helium has long been used as a testing ground for understanding correlation phenomena.

Despite the importance of the problem, and the abundance of widely varying theoretical predictions at all energies, available data are definitive only for a few eV above the double-ionization threshold (79 eV), where the ratio of double-to-single ionization of helium has been shown to be in good agreement with Wannier Theory. At high photon energies, theoretical predictions vary by a factor of two, and few data exist in this region. At energies above a few keV, photoionization is gradually supplanted by Compton ionization as the dominant ionization process. Only recently have theories begun to address this process in double ionization. It was the goal of our work on X25 to obtain an accurate the energy-dependent ratio of double-to-single ionization of helium from a few keV to 20 keV.

Figure 1 illustrates a spectrum obtained at 20 keV, showing both charge states of helium. Care was taken to assure that low energy light from the monochromator or collimating slit assemblies was filtered from the beam. Our measured ratios (Fig. 2, J. C. Levin, G. B. Armen, and I. A. Sellin, Phys. Rev. Lett. 76, 1220 (1996)) suggest that an asymptotic ratio of double-to-single ionization is not yet reached at 20 keV, much later than predicted by some theories.

Figure 1. Time-of-flight spectrum of helium obtained with 20 keV photons.

Figure 2. Comparison of present results with several recent theoretical predictions.

* Work supported by NSF

J. L. Libbert, I. K. Robinson, (Univ. Illinois), R. Pindak, R. M. Fleming (AT&T), S. B. Dierker (Univ. Michigan)

We have examined the reflectivity from several oxidized Si (111) surfaces illuminated by a coherent x-ray beam. We were able to demonstrate that the coherent x-ray diffraction (CXD) technique is sensitive to the distribution of steps on these surfaces and the 'motion' of these steps. The x-ray reflectivity of a rough surface displays both a specular and a diffuse, non-specular component which is related to the distribution of steps on the surface[1]. Under CXD conditions the non-specular component will exhibit fine structure related to the specific arrangement of the steps on the surface. Motion of the steps will change the detailed appearance of the 'speckle' pattern. Figure 1 shows three speckle patterns from slightly different areas of an oxidized Si(111) surface each taken after shifting the illuminating beam by less than its width, simulating motion of the steps. These scans were taken at $q=0.09 \text{ \AA}^{-1}$ by scanning a $20 \text{ }\mu\text{m}$ pinhole located 1.25 m behind the sample across the reflected beam from a $5 \text{ }\mu\text{m}$ source aperture. Changes of the speckle pattern with time, similar to those seen in Fig. 1 can be expected if the surface steps are caused to move as during growth or etching situations. By studying the time dependence of these changes it should be possible to deduce the step diffusion rates of the processes. Figure 2 shows changes in a speckle patterns due to etching a Si surface with a buffered HF solution. [1] S. K. Sinha, et. al. Phys. Rev. B, 38, 2297 (1988)

Figure 1.

Figure 2.

K.V. O'Donovan, M.B. Salamon (UIUC), B.A. Everitt (NVE, Inc.), T. Thurston, D. Gibbs and L. Berman (NSLS)

In the course of a search for evidence of an induced spin density wave in the non-magnetic Lu layers of Dy/Lu superlattice, we have discovered an asymmetry in the response of even- and odd-order superlattice harmonics to temperature and resonance conditions near the Lu L_{III} edge. To discern the weak signals generated from XRES in the presence of charge scattering from superlattice harmonics, we used a polarimeter employing an MgO crystal, whose (420) planes present a Bragg angle of 45.4° at the Lu edge, to measure the σ -to- π channel of the scattered radiation from the low Q side of the (0004) Bragg peak. While the X25a wiggler radiation is strongly σ -polarized, the π component gives rise to charge scattering that obscures any magnetic signal. Lorentzian fits to the 2nd order and 3rd order superlattice sidebands, measured over a temperature range from 20 K to 200 K and slightly off the Lu L_{III} resonance (9.240 keV and 9.295 keV) revealed the difference in response of these two peaks. As Figure 1 shows, the 2nd order peak exhibits an enhancement by a factor of four at low temperatures, whereas the 3rd order peak shown in Figure 2 changes by less than a factor of two. However, over the same temperature range, moving off-resonance reduces the 3rd order peak by a factor of two to three; the 2nd order peak decreases by only a factor of 1.5 upon moving off-resonance. Odd-order peaks in a superlattice are most sensitive to differences in the atomic scattering factors of the constituent elements, while even-order peaks mainly reflect the different thicknesses of the component layers. The strong temperature dependence of the 2nd order peak is due to magnetostriction that accompanies magnetic order. The ordinate in these figures has units of counts/ 5×10^5 monitor counts. Despite the weakness of these signals, they dominate the magnetic scattering; their temperature and energy dependence makes extraction of the magnetic component difficult at this stage.

Work performed at Brookhaven is supported by the USDOE under contract EDAC02-76CH00016. University of Illinois research is supported by NSF Grant DMR-94024339 and DOE grant DEFG02-91-ER45439.

Figure 1. Lorentzian fits to data taken off-resonance at 9.295 keV. The right peak is the 2nd order superlattice peak on the low Q side.

Figure 2. Same configuration as Figure 1, but these fits are to data taken on resonance at 9.240 keV.

M.J. Regan, P.S. Pershan (Harvard), O.M. Magnussen, B.M. Ocko (BNL), M. Deutsch (Bar-Ilan Univ., Israel), L.E. Berman (NSLS)

In liquid metals the delocalization of the near surface conduction electrons coupled with the dominating Coulombic interactions suppresses positional fluctuations of the near surface ion cores. As a result, it is predicted that the top several layers of atoms parallel to the surface will be ordered, resulting in a damped oscillatory electron density profile, in contrast to the monotonic profile of non-metallic liquid surfaces. Although this prediction is now over two decades old, it was hitherto not rigorously tested experimentally in spite of efforts by a number of groups. In this report period we have used x-ray reflectivity to unambiguously demonstrate surface-induced layering in liquid gallium[1] and mercury[2] with atomic-scale resolution.

The main results for liquid Ga are contained in fig. 1 and provide clear evidence that a surface induced atomic layering exists. These features are consistent with an extremely flat liquid/vapor interface, layer spacing similar to the Ga atomic dimensions, and layering that extends into the bulk a $1/e$ length of 3 atomic diameters (6-7 Å).

We have also carried out measurements of the Ga surface between 24 and ~180 C. The large change in reflectivity that was measured shows no appreciable variation in the width of the peak, indicating that the layering decay length is unchanged. However, the amplitude of the density variation is clearly reduced presumably through increased capillary wave roughness.

* This work has been supported by grants from the DOE, DE-FG02-88-ER45379 and DE-AC02-76-CH00016, and the NSF, DMR-94-00396 and DMR-91-13782.

[1] M.J. Regan et al., Phys. Rev. Lett. 75, 2498 (1995).

[2] O.M. Magnussen et al., Phys. Rev. Lett. 74, 4444 (1995).

Figure 1. Measured x-ray reflectivity, normalized to the Fresnel theory, for liquid gallium at room temperature. Inset shows the best-fit density profile.

Figure 2. Normalized reflectivity data for liquid gallium at room and elevated temperatures.

I. K. Robinson, J. L. Libbert (University of Illinois), R. Pindak, R. M. Fleming (AT&T), S. B. Dierker (University of Michigan), B. Yu and D. L. D. Caspar (Florida State University).

We sought to evaluate the possibility of using coherent diffraction to investigate dynamical fluctuations in protein crystals. Protein crystals are now widely believed to be made up of multiple molecular conformations, and fluctuations between these states may be of biological relevance.

We examined a crystal of cubic insulin mounted in a glass capillary in contact with saturated mother liquor. By rapidly aligning the crystal by means of its square {100} faces, we examined the strong 002 reflection using a 5 μm incident beam and a 20 μm analyzer pinhole at 1.3m to achieve laterally coherent diffraction conditions. The X25 W/B₄C multilayers gave us an incident flux of 10⁷ per sec with sufficient temporal coherence to reach the 002 reflection at 2θ = 1.1°.

The results indeed show a multiply peaked structure in scans across the diffracted beam in the horizontal direction (2θ is vertical). The full-width of the peaks is roughly equal to the 90 μm expected for the central Fraunhofer diffraction maximum. Analogous structure was seen in the vertical direction, parallel to 2θ (data not shown). However, this pattern was not stable: the notation "A,B,C,D" shows the same scan executed at a sequence of positions on the sample separated by 10 μm horizontally. In particular, scans "A" and "C" were at the same place, but show strong differences. After this series was taken, little further 'life' remained anywhere in the sample. It is therefore not clear whether the observed effects were caused by radiation damage or not, so a future experiment with 'immortal' crystals using a cryocooler is planned.

Figure 1. Coherent diffraction patterns recorded from different parts of a cubic insulin crystal.

Spin-polarized XANES of First Metalloprotein – Demonstration with Rubredoxin	X25
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X. Wang, A. Froeschner and S.P. Cramer

During our fall beamtime, we conducted high resolution $K\beta$ fluorescence experiments at Fe K-edges using spin state selective detection. We have successfully measured first $K\beta$ emission spectrum and spin-polarized X-ray Absorption Near Edge Structure (XANES) of an Fe protein, *pf.* Rubredoxin. The $K\beta$ emission spectra for high-spin oxidized Rubredoxin, excited at 7200 eV, are shown in Fig. 1. The spectrum is split into two regions. The main peak (known as $K\beta_{1,3}$) is found at around 7057.5 eV, while the satellite ($K\beta'$) is at 14 eV lower energy side. The spin-polarized XANES are shown in Fig. 2. The spin-down edge is measured by monitoring the fluorescence at the $K\beta$ peak and the spin-up edge at the $K\beta'$ region. The difference between the spectra is clearly shown in the pre-edge region. In the spin-down spectrum, there is a strong feature about 9 eV below the edge, which can be assigned to $1s \rightarrow 3d$ transitions, while there are not any distinct features in the spin-up spectrum. For high-spin d5, all the spin-up states were occupied while 5 spin-down states are still available. When monitoring spin-up transitions (selecting $K\beta'$), there are no transitions allowed by the spin-selection rules, while spin-down transitions (detecting at $K\beta$) are allowed. The $K\beta$ detected edge also shows sharper features when compared to the regular K-edge (detected by transmission or total fluorescence) since the lifetime broadening of $1s$ core hole is eliminated.

There is some fine structure on the pre-edge features, which may correspond to the splitting between the t_{2g} and e_g levels (10 Dq is assigned as the energy difference) in tetrahedral symmetry, is not seen in normal absorption edges since the 10 Dq (around 1.1 eV) is buried within the $1s$ core hole lifetime broadening (1.25 eV). There are also more features on the top of the absorption edges, not visible in the normal K-edge, which will require more extensive analysis.

Each of the protein spectra presented below are the result of between 5 and 7 hours of signal averaging, with the exception 15 hrs of spin-up XANES spectra.

Figure 1. $K\beta$ emission spectrum of Rb. Figure 2. Spin-polarized XANES of Rb.

Complex of elongation factors EF-Tu and EF-Ts	X25
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Y. Wang (Yale University), Y. Jiang (Yale University), M. Sprinzl (University of Bayreuth), P. B. Sigler (Yale University and HHMI)

The structure of the complex of bacterial elongation factors Tu and Ts has been studied by xray crystallography. The structure determination of the complex will provide important information on the mechanism of nucleotide exchange in elongation factors and other members of the GTPase superfamily. A native crystal of the complex has been measured to 3 Å at the X25 beam line of NSLS. It has a $P2_1$ form with $a=120$ Å, $b=127$ Å, $c=123$ Å, $\beta=90.3$. At present time derivative crystals are under study to solve the structure.

Glancing-Incidence X-Ray Magnetic Scattering Studies of the UO_2 (001) Surface	X22C, X25
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G. M. Watson, Doon Gibbs (BNL), G.H. Lander, H. J. Matzke (EITU), B.D. Gaulin (McMaster), L.E. Berman (BNL) and W. Ellis (SNL)

Traditionally, x rays have been used as a probe of the atomic structure in condensed matter. As was first shown by de Bergevin and Brunel[1], x rays can also be used to study magnetic structures. However it is the enhancement of the magnetic scattering cross section when the incident photon energy is tuned to an absorption edge that has made x ray scattering an especially useful probe of magnetic structures. Here we present the first resonant x-ray scattering measurements of the magnetic structure near an interface, obtained under glancing-incidence conditions.

In Figure 1, the scattered intensity along the $(10L)$ magnetic truncation rod of the (001) surface of the simple antiferromagnet UO_2 is shown. Data was obtained with the incident x ray energy tuned to the U M_{IV} edge at 3.728 keV. The line indicates the best fit to a model consisting of the ideal, bulk-truncated, magnetic structure, and includes Fresnel effects. We find that the scattering shown in Fig. 1 exhibits an enhancement when the incident photon energy is tuned to the resonant condition, as expected. Remarkably, scattered intensity at grazing-incidence appears to continuously vanish at the bulk Neel temperature. This is in contrast to the bulk magnetic order which is strongly discontinuous.

[1] F. de Bergevin and M. Brunel, Phys. Lett. 39A, 141 (1972).

Figure 1. Intensity of the $(10L)$ magnetic truncation rod measured at three temperatures below the bulk Neel temperature of 30.2 K. Inset: Transverse scan through the $(10L)$ rod at $L = 0.06$.

Micro-XAFS investigations on aqueous metallic species in fluid inclusions up to 430°C	X26A
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Alan J. Anderson (St. Francis Xavier Univ., Canada), Robert A. Mayanovic (Southwest Missouri State Univ.), Saša Bajt (U. of Chicago)

The x-ray microbeam capability of this beam line was used to collect XAFS spectra from aqueous zinc species in individual fluid inclusions at elevated temperatures. The fluid inclusions examined in this pilot study occur in quartz and are typically less than 100 μm in their longest dimension. Synchrotron x-ray fluorescence (SXRF) and microthermometric analyses indicate that the studied inclusions contain metalliferous (Mn, Fe, Zn, Pb, Sb) chloride brines with a salinity of about 35 wt% NaCl equivalent. Zn K-edge micro-XAFS measurements were made on a single fluid inclusion at temperature intervals of approximately 50 degrees, ranging from room temperature to 430°C. Examples of the XAFS spectra collected from test solutions and high temperature fluid inclusions are shown in the figure below. The x-ray optics included using a single Si(111) channel-cut monochromator, an 8:1 Al(Pt coated) focusing mirror, and a pinhole aperture positioned at the focal plane. The XAFS spectra were collected in the fluorescence mode using a Si(Li) detector. A programmable heating stage mounted on the X-Y-Z- mobile stage of the x-ray microprobe beam line was used to heat the sample.

Initial results indicate that the tetrahedral chlorozinc(II) complex, $ZnCl_4^{2-}$, is the dominant aqueous zinc species in the fluid inclusions up to 400°C. This result is surprising in view of previous solubility studies which indicate that the neutral complex $ZnCl_2 \cdot 0$ is dominant at temperatures greater than 300°C in solutions in the 0.5-5.0 M total chloride range. Reasons for this discrepancy are currently under investigation.

We have demonstrated that structure of metal complexes in high temperature solutions can be obtained directly by using the micro-XAFS technique on individual fluid inclusions. This method may be applied to studies of synthetic fluid inclusions of known composition, in order to provide new insights on metal complex stability and coordination in high temperature-high pressure aqueous electrolyte solutions. Such studies are important for understanding the thermodynamics of metal complexes in hydrothermal fluids occurring in crustal rocks, nuclear reactors, and geothermal power generators.

Chemical Speciation of Uranium in Contaminated and Chemically Remediated Soils by Micro X-ray Absorption Spectroscopy *

X26A

P. M. Bertsch, D. B. Hunter, and P. R. Nuessle (University of Georgia)

Employing spatially resolved XAS and X-ray fluorescence (SXRF) spectroscopy we have investigated the distribution and chemical speciation of U in contaminated soils and sediments. X-ray absorption near edge structure (XANES) spectroscopy demonstrated significant spatial heterogeneity in the oxidation states of U in the samples that was clearly discernible on a 20 to 100 μm scale. As a result of this spatial heterogeneity, we developed a three point calibration method to rapidly determine U oxidation states. The total counts obtained with the monochromator positioned at the U(IV) edge were divided by the total counts when the monochromator was positioned at the maximum of the U(VI) white line, i.e., 12 eV above the U(IV) edge, with both being normalized to the background collected at ~ 50 eV below the absorption edge. The reproducibility in the ratio obtained for 11 replications of the U(IV) and U(VI) reference samples was $\text{UO}_2(\text{c}) = 0.55 \pm 0.03$ and $\text{UO}_2^{2+} = 0.25 \pm 0.01$. This enhances the ability to collect oxidation state information at much lower U concentrations in a reasonable time frame and allows for the examination of hundreds of individual grains or for the generation of oxidation state distribution maps at a 20 μm spatial resolution. Experiments conducted on a thin section of mixed U containing mineral phases where full XANES spectra were also collected on selected regions confirmed the ability of the method to delineate proportions of U in different oxidation states (Figure 1). This experimental approach is currently being applied to U contaminated soils to evaluate the efficacy of a number of lixiviants and other chemical remediation technologies.

* This research was supported by contract DE-ACO9-76SROO819 between the University of Georgia and the U.S. Department of Energy

Quantitative microanalysis of oxidation state ratios in complex silicate minerals - (I) Fe in amphibole

X26A

J. S. Delaney (Rutgers U.), M. D. Dyar (West Chester U.), S. Bajt and S. R. Sutton (CARS, U. of Chicago)

The amphiboles are chemically and crystallographically among the most complex of the silicate minerals found in common rock types. Unlike many common minerals amphibole can have ferric/ferrous iron ratios varying between 0 and 1 depending on the substitution of H^+ into the crystal lattice. The samples studied here have bulk ferric/ferrous ratios varying from 0.18 to 1.0 determined previously by Mössbauer spectroscopy [1] and wet chemistry [2].

Synchrotron microXANES (SmX) analyses of the ferric/ferrous ratio made in 50x30 micrometer areas, and the Mössbauer and wet chemical bulk analyses agree well. The SmX technique uses the position of the pre-edge feature of the Fe K-absorption XANES spectrum [3] and the ferric/ferrous ratios of amphiboles were calibrated against both the Mössbauer data and an independent linear calibration based on ratios in pure hematite (1.0), magnetite (0.67) and synthetic fayalite (0.0) [3]. Comparison of results from the two techniques shows good consistence between microbeam and bulk techniques and suggests that the influence of the crystal structure on the XANES pre-edge of the amphibole minerals is minimal. Systematic variation of ferric/ferrous ratios within a single amphibole crystal was repeatedly observed and identified as oxidation state zoning.

This represents the first microanalytical measurement of oxidation state variation within a single natural crystal. Ferric/ferrous ratios in complex minerals such as amphibole can be reliably measured with nearly comparable spatial resolution to microanalysis techniques used for major element abundance determination. The demonstrated ability to measure zoning in crystals permits to monitor the influence of oxygen and water fugacity changes during the crystallization of amphibole in natural silicate systems for the first time. Synchrotron microXANES analysis of oxidation states in mineral systems provides a powerful new tool for studying natural crystallization environments.

References: [1] Dyar et al. (1993) *Amer. Mineral.* 78, 968.

[2] Cosca et al. (1991) *Contrib. Mineral.Petrol.* 108, 472.

[3] Bajt et al. (1994) *Geochim. Cosmochim. Acta* 58, 5209.

In-situ detection and chemical analysis of extraterrestrial material captured in aerogel *

X26A

George J. Flynn (SUNY at Plattsburgh), Saša Bajt and Stephen R. Sutton (CARS, U. of Chicago)

Low density silica aerogel has been used for the intact capture of micrometeorites and space debris on earth orbital satellites and it is the capture material proposed for the "Stardust" cometary flyby and sample return mission. Typical 5 to 50 micron extraterrestrial particles and earth orbital debris are decelerated in the aerogel, and come to rest several millimeters beneath the surface. In-situ chemical analysis is desirable to determine which of the captured particles are space debris (typically composed of Al, Al-oxide, or metals) and which are extraterrestrial (typically of chondritic meteorite composition).

Six fragments of the Allende meteorite, each 30 to 50 microns in size, were captured in a silica aerogel of density 20 mg/cc, after being shot at the aerogel at about 3 km/sec. These fragments were buried at depths ranging from 1.1 to 4.9 mm below the surface of the aerogel.

We examined these six fragments using the X-ray Microprobe at Beamline X26A. They were located using the video-microscope imaging system, and x-ray fluorescence spectra were acquired. The fluorescence x-rays are attenuated by passage through the aerogel, thus the sensitivity for low-Z elements decreases with increasing burial depth. We detected Cr, Ni, Fe, Cu, and Zn in all six particles, but detected Ca only in the particles buried to less than 3.6 mm, and detected a very weak Al fluorescence only in the particle buried at 1.1 mm.

The detection of the volatiles Cu and Zn provides an unambiguous way to distinguish between man-made steel fragments (orbital debris) and chondritic micrometeorites (which have abundant Zn and Cu). The in-situ detection and analysis of Allende fragments demonstrates that in-situ analysis of aerogel capture cells flown on earth-orbiting satellites or on cometary flyby/sample return missions is feasible using the X-Ray Microprobe at Beamline X-26A.

* This work was supported by NASA Planetary Materials and Geochemistry grant NAG-9-459 (GJF) and NAGW-3651 (SRS)

TRACE ELEMENT MEASUREMENTS IN INTERPLANETARY DUST *

X26A

George J. Flynn (SUNY at Plattsburgh), Saša Bajt, and Stephen R. Sutton (CARS, U. of Chicago)

As part of a continuing study of the chemical composition of interplanetary dust particles (IDPs) recovered from the Earth's stratosphere by NASA, we measured the abundances of elements from Cr to Sr in 13 large IDPs (each 35 to 50 microns in size) using the X-ray Microprobe at Beamline X-26A. The average composition of these 13 large IDPs is very similar to the composition of the CI chondritic meteorites, which are believed to represent the solar composition. The averages of the volatile elements Cu, Zn, Ga, Ge, and Se all within about 20% of the CI composition in this set of large IDPs. This is distinctly different from the results we have previously measured on 51 smaller IDPs (generally 10 to 20 microns in size), which show enrichments of the volatiles Cu, Zn, Ga, Ge, and Se by factors of 1.5 to 3 over CI (1). This suggests large IDPs which are strong enough to resist fragmentation on collection, are chemically different from typical smaller IDPs, and may reflect a difference in the source(s) being sampled by the two types of IDPs. A subgroup of the smaller IDPs (9 of 51 particles) have a composition similar to CI meteorites and these large IDPs (1).

Bromine is enriched relative to the CI meteorites in most of these large IDPs as it is in the smaller IDPs (1). We observed that two Br-rich IDPs (Br >300 ppm) which were each analyzed twice showed about a factor of two Br loss between the first and second analyses, presumably due to sample heating during the first analysis. In follow-up experiments on 5 Br-rich IDPs, we demonstrated that, over a 2-hour period of exposure to the x-ray beam, a roughly exponential loss of Br occurs. After this period the Br concentration remains constant for beam exposures of up to 12 hours. Since the beam heating is small, the observations suggest there are 2 types of Br in these IDPs, a very weakly bound Br component, possibly Br surface contamination, and a more strongly bound Br component, presumably bound in a mineral phase. No loss of Zn or Cu was observed, indicating they are more strongly bound than the Br. Experiments to determine if Cl and S are also lost are presently in progress.

REFERENCES: 1. Flynn, G.J. et al. (1993) Lunar and Planet Sci. XXIV, 495-496.

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Sorption of iodine species on some minerals

X26A

Mark Fuhrmann (BNL), Saša Bajt (CARS, U. of Chicago), Martin Schoonen (SUNY at Stony Brook)

This study represents part of a systematic experimental research program to investigate the interactions between aqueous iodine species and geomaterials. In this abstract we report the development of a XANES technique to examine the speciation of iodine in solutions on mineral surfaces in contact with those solutions.

Using XANES we determined the speciation of iodine in solution and on the surfaces of minerals in contact with several iodine solutions. The analysis was performed at the synchrotron x-ray microprobe beam line X26A. The iodine L_3 edge is at 4.557 keV which is close to the low hardware limit (4 keV) of the Si(111) monochromator. By enclosing the whole end of the beamline in a plastic bag filled with He gas, the flux of the x-rays was almost the same as if the x-rays were in vacuum. The low energy of the iodine edge and interferences caused by some other elements (the most troublesome was Ca) required use of solution concentrations of iodine that are much higher than those found in the environment.

Having established that iodine speciation was discernible through XANES, we were then able to examine its speciation on minerals and solutions in contact with them. Intensity of the iodine signal above the absorption edge obtained in fluorescence mode was used to determine the concentration of iodine in the liquid and on the solid of each sample.

Magnetite sorbed iodide from solution but not iodate. Biotite, in contrast, sorbed iodate from the buffered solution but did not take up any iodide. In neither case was sorption accompanied by any obvious change in speciation. However, there is a slight change in the scan on iodide on the solid phase of magnetite in which the 6 eV shoulder is less distinct than in the reference solutions. This may represent a mixture of iodide and iodine on the magnetite surface while the solution in the same cell contains iodide.

In the pyrite/iodate system, iodine was removed from solution accompanied by reduction from iodate to iodine in both solid and liquid phases. Significant sorption resulted in the very low value for $I_{L/S}$ (intensity of the iodine signal in the liquid divided by its intensity on the solid) of 0.5. The pH was lowered to 4.1 by dissolution of the pyrite surface, even though the solution was buffered. Iodine speciation can be controlled by pH and this is probably the case here, but there was a strong signal from I_2 given by the slurry indicating sorption. In the pyrite/iodide system there was no sorption and no change in speciation in either the liquid or the slurry. The high value of $I_{L/S}$ indicates that iodide is enriched in the supernate compared to the slurry, the result of ion exclusion caused by overlapping charge fields of mineral grains repelling the similarly charged iodide ion.

Investigation of the pre-edge absorption XANES structure

X26A

Albert L. Hanson (BNL), and Saša Bajt (CARS, U. of Chicago)

The pre-edge scattering of x rays is being studied with a high energy resolution wavelength dispersive spectrometer to determine how valence states of the scattering atoms can be extracted directly from the scatter spectra. At an energy of a few electron volts below the absorption edge of iron, spectra from iron in the +3 valence state exhibit peaks characteristic of resonant, inelastic scattering. However, if the iron exists in the +2 valence state, there are no peaks characteristic of the resonant, inelastic scattering. Because of the substantial differences in the scatter spectra between iron in the +2 and the +3 valence states, this scattering is a promising technique for quantitative analyses of the valence states. Present effort is to determine the accuracy of such an analytical technique.

Micro-XANES of iron redox states in wood during degradation by fungi *	X26A
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B. L. Illman (U. of Wisconsin, Forest Products Lab), S. Bajt (CARs, U. of Chicago), P. Nussle (SRFL, U. of Georgia)

The fundamental mechanism by which fungi degrade wood is not clearly understood. Knowledge about the mechanism is needed to develop more environmentally compatible strategies to prevent the economic losses of wood to decay. Current theories propose a role for Fe in the decay process [1]. The lack of a non-intrusive system to detect and measure Fe redox states in situ has hindered the progress of determining Fe reactions during decay. A method to detect Fe in situ in wood during decay by fungi has been developed using synchrotron X-ray fluorescence spectroscopy (SXRF).

The SXRF micro-probe on beam line X26A at NSLS was used to detect Fe in southern yellow pine wood during decay by several species of basidiomycetous fungi. Metal redox states were determined on a small scale of 150 microns by measuring X-ray absorption near-edge structure (XANES). The Fe^{2+} to Fe^{3+} ratio was determined by using an established microXANES technique [2]. Due to the high concentration of Mn in wood and the low concentration of Fe, a computer code was used to extract the Fe K α peak from much more intense Mn K β peak.

We found that Fe^{3+} is the primary redox state in sound wood, that the concentration of total Fe was higher in wood inoculated with fungus than in sound wood, and that the ratio of Mn to Fe are lower in decayed wood than in the sound wood. The ratio of Fe^{2+} to Fe^{3+} in wood inoculated with *Positia placenta* was 1:4, indicating that the fungus had reduced 28% of the Fe. The results confirm that fungi mobilize Fe, bringing Fe into the wood during decay, and that Fe redox reactions occur during the decay process. This in situ method will be the foundation on which we test the effects of Fe chelators, oxidants and reductants on the decay process and expand our knowledge about the role of Fe in the mechanism of decay.

[1] Illman, B. 1991. Active Oxygen/Oxidative Stress and Plant Metabolism, B.J. Fell, K.L. Steffen, J.C. Shannon, eds. Am. Soc. Pl. Physiol. pp 97-106.

[2] Bajt, S., Sutton, S.R., and Delaney, J.S. (1994), GCA 58, 5209-5214.

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H. S. Isaacs and S-M. Huang (BNL)

Behavior of Dissolved Molybdenum during Localized Corrosion of Austenitic Stainless Steel	X26A
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Molybdenum leads to marked improvements in the corrosion resistance of stainless steels and differing models of action have been proposed for the reduction of corrosion. A number of models have proposed that Mo forms a salt layer during the dissolution of the steel. Salt layers have for the first time been observed using energy dispersive x-ray techniques and has now been used for an in situ study of the chemistry of molybdenum during localized corrosion of stainless steel in chloride solutions. An artificial pit was formed by dissolving back the cross section of a 15 micron thick strip of Type 316 stainless steel foil mounted in an epoxy resin. A high intensity diameter polychromatic x-ray beam at Beamline X26A was scanned across the steel, a salt layer on the steel, and the concentrated dissolution products within the artificial pit. The resulting x-ray fluorescence was analyzed to determine changes in concentration of the constituent alloying elements. It has been found that the salt layer on the steel was formed mainly by iron chloride and all other alloying elements were present at relatively lower concentrations than the steel. Virtually no chromium remained in the salt layer. Also, little molybdenum was present negating proposed corrosion inhibition by a definitive molybdenum forming salt layer. Within the concentrated artificial pit solution it was found that alloying elements dissolved and migrated down a concentration gradient, but closer to the mouth of deep (≈ 2 mm) pits, precipitation of molybdenum occurred to a minor extent that did not affect the localized corrosion processes.

X26A

P. A. Northrup, and R. J. Reeder (SUNY at Stony Brook)

Synchrotron X-Ray fluorescence microanalysis has been used to investigate the three-dimensional spatial distribution of compositionally distinct growth sectors and subsectors in mineral crystals. In these experiments, fluorescence emissions are activated by the incident beam penetrating through the sample section, but are only detected from an "effective sampling depth", beyond which emissions are re-absorbed by the overlying sample material. The effective sampling depth differs for each element in a given substrate, depending on the characteristic energy of the fluorescence photon. This seeming disadvantage can be utilized to characterize the interface between two sectors or subsectors at depth in the sample if they possess distinct differences in the concentrations of two or more suitable elements. Moreover, this technique is nondestructive; alternative methods of analysis commonly require progressive sectioning or polishing through a sample.

During growth, several minerals differentially incorporate trace elements into regions of a single crystal that formed contemporaneously but under structurally nonequivalent surfaces. These sectors and subsectors preserve a record of surface processes and growth mechanisms as growth progresses, in much the same way that concentric zonation preserves a record of crystal morphology. Application to topaz ($\text{Al}_2\text{SiO}_4\text{F}_2$), in which surface-controlled trace element partitioning associated with surface growth step orientations on spiral-growth hillocks creates a patchwork of sectors and subsectors, utilizes trace Ti, Fe, and As (with effective sampling depths of approximately 30, 65, and 400 μm , respectively). This approach can provide useful information about the contrasting growth mechanisms on different crystal forms, and thus far has identified significant differences in growth kinetics between (110) and (111).

Further measurements of trace element zoning patterns show that there are both important similarities and enlightening differences between samples from different localities. In addition, SXRFMA data is currently being applied to growth-surface modeling studies, with the goal of explaining topaz crystal growth on a molecular scale.

A Time Resolved *In Situ* XANES Study of Surface-Enhanced Reduction of Smectite Structural Fe by Organoborates *

X26A

P. R. Nuessle, W. P. Gates, D. B. Hunter, and P. M. Bertsch (University of Georgia)

Previous investigations demonstrated that the sorption of tetraphenylboron (TPB) to smectitic clay minerals was followed by surface facilitated degradation via both bronsted acid hydrolysis and lewis acid pathways. The kinetics of surface-enhanced TPB degradation measured on smectitic clay minerals having a range of structural Fe by *in situ* Fourier transform infrared (FTIR) spectroscopy, indicate that structural Fe may be involved as an electron acceptor in the two-electron transfer of the lewis acid degradation pathway. An *in situ* time resolved X-ray absorption near edge structure (XANES) spectroscopic study was conducted to test this hypothesis and to provide more specific information on the role of structural Fe on surface facilitated oxidation reactions. The Fe K α absorption edge was observed to shift to lower energies following addition of TPB to the clay suspensions and the reaction kinetics were well described by the first order degradation rate models previously derived from the FTIR data (Figure 1). Associated changes in both edge and pre-edge features accompanied the reaction, also revealing that structural Fe was reduced concurrent with the oxidation of TPB. Differences in both the magnitude and rate of edge shifts, as well as the ratios of the fluorescence intensities at +4.8 and +6.9 eV (relative energies) indicate that: (i) a portion (15-20%) of nontronite structural Fe was reduced; (ii) nearly all (>95%) of montmorillonite structural Fe was reduced; and (iii) on an absolute basis, similar levels (0.6 mmol g⁻¹) of structural Fe were reduced in both smectites (Figure 2). Ongoing investigations are examining the reversibility of these environmentally relevant surface-facilitated organic degradation reactions.

Figure 1.

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Figure 2.

REE intrasectional zoning in apatite, determined using synchrotron x-ray fluorescence microanalysis (SXRFMA)	X26A
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J. Rakovan, and R. J. Reeder (SUNY at Stony Brook)

Intracrystalline REE distributions in fluorapatite have been studied using cathodoluminescence and synchrotron x-ray fluorescence microanalysis (SXRFMA). In the apatite samples studied the face grows by the spiral mechanism. As a result, polygonized growth hillocks with three vicinal faces occur on (1010). Face symmetry, *m*, constrains the [011] and [01 $\bar{1}$] growth steps to be equivalent. However, [001] steps are not symmetry related. REE and Mn cathodoluminescence qualitatively indicates a differential distribution of Mn²⁺, Sm³⁺, Eu³⁺, and Eu²⁺ between subsectors associated with symmetrically nonequivalent vicinal faces (intrasectional zoning). SXRFMA shows that the concentrations of all the REEs analyzed (La, Ce, Pr, Nd, Sm, Eu, Dy, Ho, and Y), except Eu, exhibit a sharp step function, with the change in concentration correlated directly to the boundary between nonequivalent vicinal faces and associated subsectors. La, Ce, and Pr are enriched in the <011> subsectors, and REEs heavier than Pr, except Eu, are enriched in the [001] subsector. Differential incorporation due to growth rate anisotropies is inconsistent with the observed differential partitioning of REEs, supporting the proposal of Rakovan and Reeder (1994) that differences in the atomic structure between [001] and <011> steps leads to differential incorporation in apatite. Atomic scale models of the structure of these steps show qualitative differences that are consistent with this proposal. The reversal in the REE partitioning trend between Pr and Nd suggests an ion size effect on the partitioning between nonequivalent steps.

The differential distribution of REEs indicates nonequilibrium partitioning. Site specific controls on the partitioning of REEs indicate that partition coefficients are a function of surface structure and dependent on the spatial segregation of nonequivalent surface sites. Hence, different REE partition coefficients exist for incorporation at structurally different growth steps.

Chromium Leaching versus Oxidation State for a Contaminated Solidified/Stabilized Soil	X26A
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Terry L. Rinehart, Darrell G. Schulze (Purdue Univ.), R. Mark Bricka (US Army Corps of Eng.), Saša Bajt (Univ. of Chicago), and Ernest R. Blatchley, III (Purdue Univ.)

The toxicity, solubility, and mobility of chromium in soil are strongly dependent upon its oxidation state. Solidification/stabilization (S/S) is a potential method for preventing Cr leaching from contaminated soil. We evaluated the leaching behavior of untreated and solidified/stabilized Cr contaminated soil samples obtained from two locations at a military facility in Louisiana. The leaching of Cr, as measured by the Toxicity Characteristic Leaching Procedure (TCLP), was expected to be dependent upon the Cr oxidation state. The pH, cation exchange capacity and particle size distribution were obtained for each sample and portions of each sample were solidified with Type I Portland cement. The oxidation state of Cr was determined by x-ray absorption spectroscopy (XAS). The sample from Site 1 contained 478 mg/kg total Cr while the sample from Site 2 contained 1272 mg/kg total Cr.

The TCLP Cr concentration for Site 1 untreated soil was 3.4 mg/L and 2.0 mg/L for the S/S treated sample. The sample from Site 2 had TCLP Cr concentrations below the analytical detection limit (<1.0 mg/L) for both untreated and S/S samples. The XAS data showed the presence of the more mobile and soluble Cr⁺⁶ at Site 1 but not at Site 2. The use of Portland cement alone was not effective in reducing the Cr⁺⁶ to the less soluble and less mobile Cr⁺³, or in physically preventing leaching of Cr⁺⁶.

Oxidation State of Manganese in Rice Blast Fungal Lesions	X26A
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Darrell G. Schulze, Don M. Huber, A. K. M. Shahjahan, Morris Levy (Purdue Univ.), Saša Bajt (Univ. of Chicago), and Barbara Illman (USDA Forest Products Lab.)

The blast disease of rice is one of the most important plant diseases worldwide because rice is a major source of food for 60% of the world's population. Manganese is an essential mineral element for photosynthesis, lignin synthesis, and other plant metabolic functions in its Mn^{2+} or Mn^{3+} forms, but when oxidized to Mn^{4+} it precipitates as physiologically unavailable Mn oxides and hydroxides. *Pyricularia grisea* (Cooke) Sacc., the fungal causative agent of rice blast, is a strong Mn oxidizer in agar culture. Thus, fungal oxidation of Mn may be an important part of the disease processes.

We used micro x-ray absorption near edge structure (XANES) spectroscopy to compare Mn oxidation states in healthy areas of rice leaves with Mn oxidation states in blast lesions caused by *P. grisea*. Healthy tissue contained only Mn^{2+} , whereas blast lesions contained significant quantities of Mn^{4+} .

These results suggest that the ability to oxidize Mn may be a significant factor in determining the virulence of *P. grisea* and that resistant rice varieties may have developed strategies to suppress or prevent Mn oxidation by the fungus.

Real time, in-situ tracking of selenium transport and reduction across the boundary between ponded waters and sediments using micro-XANES	X26A
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Tetsu K. Tokunaga (LBL), Saša Bajt (CARS, U. of Chicago), Stephen R. Sutton (CARS, U. of Chicago), and Patterson R. Nuessle (SREL, U. of Georgia)

Contaminated transport in sediments and waters are being studied using the synchrotron x-ray microprobe and x-ray absorption near edge structure (XANES), in order to obtain direct, noninvasive, real time data on trace element concentrations. These methods are being used to test models of reactive transport which invoke the importance of micro-scale heterogeneities and processes. Many important reactions controlling chemical cycling in the environment occur at and very near the boundaries between sediments and overlying waters. The synchrotron x-ray fluorescence microprobe at the NSLS was used in monochromatic mode (micro-XANES) to obtain spatially- and temporally-resolved speciation of Se in a water-sediment system. This present study has focused on diffusion and reduction of selenium at boundaries between sediments and ponded waters.

Earlier, larger-scale experiments on transport of selenium from ponded waters into sediments indicated that reduction reactions were taking place within a few millimeters of the water-sediment boundary. In our most recent work, Se transport and reaction were studied in a 20 mm, saturated sediment column, over which waters containing Se in the form of soluble $Se(VI)$ were hydrostatically ponded. Vertical profiles through the water and sediment columns were scanned in front of monochromatic microbeams at 250 to 500 μm increments, at a set of x-ray energies which permitted determinations of Se concentrations and oxidation states. In addition, selected locations within these columns were scanned over the complete XANES region. This micro-XANES experiment permitted tracking of $Se(VI)$ reduction at pond-sediment boundaries. Results show reduction of $Se(VI)$ to $Se(IV)$, and ultimately to $Se(0)$ within specific zones in the sediments. The location of the active reduction zone was within the surface 2 mm in an extremely reducing sediment, while it was displaced several mm deeper in a less reducing sediment. These results are consistent with diffusion-limited transport calculations. The possibility that organo-Se compounds may also accumulate in reducing zones is currently under consideration. Micro-XANES results ruled out the possible formation of significant concentrations of colloidal $Se(0)$ and of organo-Se compounds in these ponded waters.

X-Ray Fluorescence Analysis With High Energy Resolution *

X26C

W.A.Caliebe(NSLS), Saša Bajt(University of Chicago), C.-C. Kao(NSLS)

X-ray fluorescence is a well established analytical technique for elemental analysis in both basic and applied research. The energy resolution of Si(Li) or Ge(Li) solid state detectors, 150 eV to 200 eV, cannot resolve the small energy shifts in fluorescence energy or changes in lineshape. Therefore, we used a high energy resolution Rowland circle spectrometer based on a Si(333) analyzer. The crystal is spherically bent to a radius of 1 m and has an effective diameter of 35 mm. In this experiment we analyzed the Cr K γ fluorescence line ($E \sim 5980$ eV) in three different oxidation states, 0, +3 and +6. The fluorescence was excited using the focused white radiation at the beamline X26C.

X-ray fluorescence lines originating from the decay of shallow core electrons or valence electrons should be particularly sensitive to the electronic structure of the sample. These fluorescence lines provide information about the occupied electronic states. The K γ fluorescence lines directly reflect changes in the valence band so that differences in the oxidation state should be directly visible in the spectra. The figure shows the K γ line of the three different Cr samples. Cr metal shows a single peak at 5988 eV, while that of Cr³⁺ and Cr⁶⁺ show additional satellite features. In comparison with that of Cr metal the energy of the main Cr³⁺ K γ line shifts by -4.4 eV while that of the Cr⁶⁺ remains at the same energy. Also, a second peak appears at 5968.5 eV for Cr³⁺ and 5972.3 eV for Cr⁶⁺. As expected, the K γ line is relatively sensitive to changes in the oxidation state. Theoretical calculations are needed for detailed interpretation of these lines. It should be noted that the fluorescence yield decreases by a factor of 7.5 from the K α to the K β line and by another factor of 20 to 30 from the K β line to the K γ line.

Figure 1. K γ fluorescence line for Cr metal, Cr³⁺ and Cr⁶⁺.

* We would like to thank Dr. Douglas B. Hunter (SREL) for preparing the chromium oxide samples. This work was partially supported by US DOE grant DE-FG02-92ER14244, DE-AC02-76CH00016 (BNL), and NASA grant NAGW-3651.

White Beam Microdiffraction for Spatially Resolved Strain, Microstructure, and Composition Mapping

X26C

G. S. Cargill III and P.-C. Wang, Columbia University, and I. C. Noyan and E. Liniger, IBM Research, together with K. W. Jones, BNL Applied Sciences

A system for strain, microstructure and composition measurements with micron or submicron spatial resolution in crystalline materials are being developed on beamline X26C. This system uses 5 to 30 keV radiation collimated and concentrated by a tapered glass capillary, together with an area CCD detector for measuring Laue patterns and an energy sensitive Si detector for measuring lattice spacings, as illustrated in Fig. 1. Novel features are that the sample being studied need not be rotated in making strain measurements, which facilitates spatial resolution on micron and submicron scales, and that polycrystalline samples can be studied with spatial resolution on the order of their grain size. This system has been used for spatially resolved strain measurements and grain orientation mapping of polycrystalline films. Two mapping modes have been used: reciprocal-space mapping and real-space mapping. For reciprocal-space mapping the sample is fixed in position (x, y) and the SSD is raster-scanned over a range of angles α and β . At each SSD position, the scattering angle $2\theta(\alpha, \beta)$ is calculated and scattered intensities are measured for energy windows of the multi-channel analyzer corresponding to various (hkl) reflections. In this way, the orientations of grains within the irradiated volume are determined. A result from such measurements is shown in Fig. 2(a). For real-space mapping, the SSD is fixed at a particular scattering angle $2\theta(\alpha, \beta)$, and scattered intensities are measured for energy windows corresponding to different (hkl) reflections as the sample position is raster-scanned in x and y . From these measurements, the locations of grains having the specified orientations are determined. Strain measurements are made using energy dispersive diffraction patterns from single grains, like that shown in Fig. 2(b).

Figure 1. Schematic of x-ray microdiffraction/microfluorescence system.

Figure 2. Diffraction from a 4 μ m thick Al (4 wt.% Cu) film. (a) An Al (111) intensity map in reciprocal space. (b) Energy dispersive diffraction pattern for detector position determined from (a), showing the (111) and (222) diffraction lines from one grain within the irradiated volume, as well as CuK α and CuK β fluorescence lines.

Search for Structural Modulations in UPt_3 Using Laue Diffraction X26C

B. Ellman, M. Sutton, L. Taillefer (McGill University), and G. Shea-McCarthy (University of Chicago)

Among the materials believed to exhibit unconventional superconductivity, UPt_3 is unique in possessing two well defined superconducting phases in zero magnetic field. Generally, the multiple phases are believed to arise from the symmetry-breaking effect of an extremely weak antiferromagnetic order parameter. With moments lying in the hexagonal plane, the AFM order would stabilize otherwise degenerate superconducting states at two different temperatures, leading to the observed behavior. However, *any* symmetry breaking field would play a similar role, including crystallographic distortions. Recent transmission electron microscopy (TEM) studies [1,2] of UPt_3 have suggested the presence of long wavelength ($\approx 60\text{\AA}$) modulations of the underlying $P6_3/mmc$ structure. In the case of single crystal whisker[1] samples (which grow spontaneously from the melt), the modulation has been shown to exist over many microns. TEM, however, requires extreme sample preparation techniques (e.g., ion milling) that might introduce artifacts. We have performed Laue diffraction measurements at X26C to try and detect the modulations. The ability of Laue experiments to cover a large volume of k-space makes them an ideal tool to search for a modulation whose exact structure is imperfectly known.

The samples were a whisker approximately $0.1 \times 0.05 \times 2\text{mm}^3$, and a larger sample cut from a bulk crystal. The data were taken using unfocused white beam and a diffuse background subtracted.

A typical diffraction pattern of the whisker, using an exposure of 5 s, is shown in Fig. 1. Careful indexing is required to identify Bragg peaks due to an incommensurate modulation in the presence of the many peaks generated by the underlying structure. The result of such an analysis is shown in Fig. 2, where only relatively intense peaks have been shown. After further analysis of this and other patterns, we will be in a position to either identify the modulation in an undisturbed sample or set a convincing limit on the presence of crystallographic symmetry breaking factors in UPt_3 .

[1] B. Ellman, A. Zaluska, and L. Taillefer, Physica B 205, 346 (1995).

[2] P.A. Midgley et al., Phys. Rev. Lett. 70, 678 (1993).

Figure 1. Laue diffraction pattern of a single crystal whisker of UPt_3 . The crystal is oriented such that the a - c plane is rotated 19 degrees about $\hat{c}$ with respect to the image plate.

Figure 2. Predicted Laue peak positions for the data of figure 1. By carefully comparing the theory and data, we may either identify or exclude reflections due to a structural modulation.

The effect of microgravity on the protein crystal growth: Concanavalin A as a case study *

X26C

G. Shoham and L. Arnowitz (University of Jerusalem, Jerusalem, Israel), V. Stojanoff and D. P. Siddons (BNL-NSLS)

The present report is part of a long range project on the study of the effect of microgravity on the growth of macromolecules. The Space Shuttle is a potential platform for growth of protein crystals of exceptional quality. Our goal with this preliminary work is to show that crystals grown under microgravity conditions present improved lattice perfection. Monochromatic as well as Laue techniques will be employed to access the crystal quality. Concanavalin A crystals grown under identical conditions except for gravity have been grown on Space Shuttle mission STS 69 (at close to 0 g) and at the laboratory (1g, Kennedy Space Center) by the membrane dialysis technique. The crystals were brought to the NSLS immediately after the Space Shuttle landing. Several methods were used to access the quality of the crystals: monochromatic x-ray topography, the Laue method, and the rotation or oscillation photography. X-ray topography showed that crystals grown under microgravity conditions present in general a smaller concentration of defects than their counterparts grown on the ground. However, different salt concentrations also affect the quality of the crystals. These results are in agreement with the diffraction data collected. Crystals grown at 0 g diffracted well beyond 1.2 angstrom resolution, while the 1 g counterparts diffracted to a resolution limit of about 1.6 $\text{\AA}$ only. The evaluation of the results is still in progress and will be divulged shortly. Nevertheless, these preliminary results strongly suggest that micro-gravity environment could be used to extend the resolution limit of protein crystals, at least in the cases when all other crystallization conditions have been optimized.

* The support of Biocars, and especially of Ms. G. Shea McCarthy, is gratefully acknowledged. This preliminary micro gravity study was made possible with the great assistance and support of IDEA and BioServe Space Technologies.

Fabrication of a mm-wave undulator cavity using deep x-ray lithography

X26C

J. J. Song, B. Lai, D. C. Mancini, A. Nassiri (APS/ANL), A. D. Feinerman (University of Illinois-Chicago), G. M. Wells, V. White (University of Wisconsin-Madison)

The possibility of fabricating mm-wave radio frequency cavities (100-300 GHz) using deep x-ray lithography (DXRL) is being investigated. The fabrication process includes manufacture of precision x-ray masks, exposure of positive resist by x-rays through the mask, resist development, and electroforming of the final microstructure. The precision DXRL mask was made by means of an intermediate mask, using soft x-ray lithography for pattern transfer into poly-methylmethacrylate (PMMA) on a 200 mm Si wafer, followed by electroplating of 25 mm Au.

For the DXRL process, PMMA was used as the positive resist, either as an 1-mm sheet or cast onto a Cu substrate. To promote better adhesion of the PMMA to the substrate, the Cu surface was modified either by growing a thin oxide film or by depositing a thin Ti coating. The NSLS X-26C beamline was used to expose the resist by scanning vertically through the beam with a computer-controlled step-motor translation stage. Exposure took place under He purge at 1 atm. The ratio of the surface dose to the bottom dose for the 1-mm-thick PMMA is about 1.5. Two different developers were used: the first is a mixture of 60% vol 2-(2-butoxy-ethoxy) ethanol, 20% tetrahydro-1, 4-oxazine, 5% 2-aminoethanol-1, and 15% DI water, and the second developer is methyl-isobutyl ketone (MIBK) diluted with 2-propanol. After developing the microstructure, it will be electroplated and the surface of the electroplated area will be finished by diamond-turning, followed by removal of the residual PMMA.

The 30- or 84-cell 108-GHz mm-wave cavities, which can serve as an electromagnetic undulator, is shown in Fig. 1. The mm-wave undulator is very attractive since it has special features compared to the conventional undulator: (1) higher photon energy since the undulator period is much smaller (typically 1-mm or less) and (2) faster tuning ability and wider tuning range since the mm-wave power is easier to handle. With the Advance Photon Source (APS) linac system, which provides a low-emittance electron beam with energy up to 750-MeV by using an rf thermionic gun, the first harmonic of the undulator radiation will be at 5.2 keV. The undulator parameters are summarized in Table I.

This work is supported by U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No W-31-109-ENG-38.

1. J.J. Song, A.D. Feinerman, Y.W. Kang, R.L. Huston, B. Lai, A. Nassiri, V. White, G.M. Wells, "Toward Fabrication of mm-Wave Undulator Cavities", submitted to Rev. Sci. Instrum.

Figure 1.

Frequency	f	108 GHz
Shunt	R	312 MΩ/m
Quality Factor	Q	2160
Peak Power	P	29.1 kW
Charge Particle Energy	E ₀	650-750 MeV
Deflection Factor	k	0.0467
Undulator Wavelength	λ	1.0 mm
Number of Periods	N	80
Length	l	8 cm
Gap Height	g	0.6 cm

Figure 2. Table I - The 108-GHz undulator parameters with the APS linac/rf gun.

Laue crystallographic studies of enzymatic intermediates: isocitrate dehydrogenase

X26C

Barry L. Stoddard, Jill M. Bolduc, and Dave H. Dyer (Fred Hutchinson Cancer Research Center, Basic Sciences Division), William G. Scott (Medical Research Council, Cambridge, England), Robert M. Sweet and Paul Singer (BNL Biology Dept.)

Site-directed mutagenesis, enzyme kinetics, and fast Laue diffraction were used to solve the structures of two different, sequential intermediates which accumulate as steady-state complexes during turnover by isocitrate dehydrogenase, and to visualize the structural mechanism of electron transfer for this enzyme.

Two kinetic mutants, which display large, unique rate barriers at separate steps of the catalytic mechanism, were used to visualize these species within the overall reaction pathway. These two site-directed mutants, Tyrosine 160 to Phenylalanine (Y160F) and Lysine 230 to Methionine (K230M), are amenable to either single-turnover or steady-state Laue experiments. Each mutant displays a wild-type rate constant for one half-reaction, but a substantial rate decrease for the other half reaction, producing two different rate-limited intermediates.

Based on the available kinetic parameters in the crystal, polychromatic x-ray diffraction data were collected from several crystals of each mutant before and after substrate binding at beamline X-26C at the Brookhaven National Synchrotron Light Source. Difference maps were then calculated with experimentally determined Fourier coefficients: [F_o (after substrate) - F_o (before substrate)] acalc, using phases calculated with protein coordinates prior to any refinement and then after an initial round of refinement against the Laue data. No substrate or water molecules were included in either phase calculation. The strongest features of the maps calculated at either stage are identical and easily modelled by the components of the rate-limited enzyme complexes. The initial R-factors for the protein model prior to refinement were approximately 30%; the R-factor after initial refinement were both approximately 19%. The final refined R-factors after inclusion of substrates and metal were 18.3% and 17.4%, respectively.

The difference map calculated for the tyrosine mutant (Y160F) indicates the accumulation of a rate-limited Michaelis complex of isocitrate, NADP⁺, and Mg⁺⁺ which is trapped prior to hydride transfer. The protein fold, active site architecture, and conformation of bound isocitrate are unchanged relative to wild type enzyme (with the exception of the side chain hydroxyl), as is the ensuing rate of enzymatic decarboxylation. The distance and orientation of the nicotinamide ring are consistent with the stereochemical transfer of the single proton from the chiral 2-R carbon of isocitrate to the re-face of the cofactor C4. Conversely, the difference map calculated for the lysine mutant (K230M) shows strong density for a bound sugar/metal complex but indicates that the nicotinamide ring and adjoining ribose and phosphate backbone of the cofactor are disordered, consistent with the conversion of the charged NADP⁺ to NADPH which is known to occur for this mutant with a rate unaffected by the mutation. The resulting rate-limited species, oxalosuccinate, has been confirmed by difference mapping and refinement is bound in a manner analogous to isocitrate; this is consistent with previous reports of oxalosuccinate acting as a catalytically competent substrate for the reverse hydrogenation reaction and the enzymatic decarboxylation.

V. Stojanoff and D. P. Siddons, Brookhaven National Laboratory, Upton, New York 11973. L. Monaco, P. Vekilov, F. Rosenberger, CMMR, University of Alabama at Huntsville.

Growth-induced defects in lysozyme crystals were studied by white beam and monochromatic X-ray topography at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL)(1-4). Single dislocations, as well as dislocation nets and highly strained regions were identified in the topographs. At least for lysozyme the topographic methods were non-destructive and regular diffraction data collection for structure determination was successfully carried out on the same crystals after the topographic observations. The temperature/supersaturation regimes during crystal growth, the defect density detected by X-ray topography, and the diffraction resolution obtainable from the crystals were all strongly correlated.

[1]Stojanoff, V., Siddons, D. P., Monaco, L., Vekilov, P. and Rosenberger, F. Submitted. [2]Stojanoff, V. and Siddons, D. P. (1995) *Acta Cryst. A* accepted. [3]Vekilov, P., Monaco, L., Thomas, B. R., Stojanoff, V. and Rosenberger, F., *Proc. ICCBM-6, J. Crystal Growth*. [4]Stojanoff, V., Siddons, D. P., Monaco, L., Vekilov, P. & Rosenberger, F. *Proceed. American Crystallographic Assn.*, abstract M132, Montreal CA, (1995). [5]Stojanoff, V., Siddons, D. P., Monaco, L., Vekilov, P. & Rosenberger, F.

Conference on Protein Crystal Growth, Panama City, USA, (1995).

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Figure 1.

Figure 2.

V. Stojanoff¹, E.H. Snell², D.P. Siddons¹ and J.R. Helliwell² - (¹BNL, ²Chemistry Department, University of Manchester, UK)

For many years a significant effort has been made towards the growth of better quality macromolecular crystals for structural studies. Usually, the quality of the crystals is inferred from x-ray diffraction data, but recently, crystal growers have been trying to employ characterization techniques that would allow direct measurement of the quality of the protein crystal.

Monochromatic x-ray topographic methods were used to compare the quality of lysozyme crystals grown in a dialysis reactor under identical conditions except for their exposure to the gravitational field. Figure 1a shows a topograph of a lysozyme crystal grown on the ground (1 g condition), and figure 1b shows the topograph of a crystal grown on board of the NASA Space shuttle IML-2 mission (0 g condition). A significant difference in the quality of the crystals was observed. The crystal grown under 0 g condition shows large quite perfect regions while the crystal grown as a control in an 1 g environment presents a high density of defects along the whole crystal.

Bosch, R., Lautenschlager, P., Potthast, L., and Stapelmann, J. (1992). *Journal of Crystal Growth* 122, 310-316; Snell, E. H., Weisgerber, S., Helliwell, J. R., Weckert, E., Hoelzer, K. and Schroer, K. (1995) *Acta Cryst D51* in press.

Related publications and presentations at conferences: V. Stojanoff, D. P. Siddons, E. H. Snell and J. R. Helliwell to be published *J. Syn. Rad.* (1995); V. Stojanoff, E. H. Snell, D. P. Siddons and J. R. Helliwell submitted to *Acta Cryst. D* (1995); E. H. Snell, S. Weisberger, J. R. Helliwell, F. Weckert, K. Holzer and K. Schoer, *Proc. ICCBM - 6, J. Crystal Growth*.

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(a)

(b)

Figure 1. Monochromatic x-ray topograph of a lysozyme crystal grown for the IML-2Space Shuttle Mission in a normal gravity condition (a) and under microgravity condition (b).

Use of Laue Diffraction Patterns in both Macromolecular and Small-Molecule Crystallography	X26C
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It has recently been shown for crystals of lysozyme and α -haemolysin that Laue data sets (collected on X26C) can be reduced to yield structure factor amplitudes of equally good quality as the best monochromatic data sets in terms of both accuracy and completeness [1]. The Laue diffraction technique could therefore be used as an extremely fast ab-initio structure determination technique, which we have tested for crystals of different small organic and organometallic compounds, both at room and liquid nitrogen temperature. Different attenuators (Zr, Br, Mo) were used for the determination of the absolute scale of the unit cell. Most of the Laue diffraction patterns could be indexed within a few minutes of the exposure using a new indexing program called laucell [2], which was helpful to judge immediately the quality of the individual crystals used.

However, the unique advantage of the Laue diffraction technique, the data-collection speed, will mainly be exploited in situations such as time-resolved crystallography. We aim to do such an experiment on the enzyme acetylcholinesterase (AChE). AChE cleaves the neurotransmitter acetylcholine (ACh) in the synapse at a very high turnover rate. The enzyme has a strong dipole moment that draws the positively charged substrate towards the catalytic site, situated at the bottom of a narrow gorge. One of the reaction products, choline, bears the same charge as the substrate, ACh, which raises the question of its route of exit from the active site.

In order to attempt to observe the reaction process, photolabile precursors of choline and of carbamylcholine (an enzymic substrate) have been synthesized [3]. These two probes generate choline in different ways, either by a direct photocleavage reaction (choline precursor) or by enzymatic hydrolysis of a substrate generated by photocleavage (carbamylcholine precursor). They constitute complementary tools for the time-resolved crystallographic studies, permitting direct monitoring of the exit of choline from the active site. So far however, both monochromatic and Laue diffraction studies have shown that crystals of AChE soaked for different times with these compounds showed high mosaicity and poor resolution, probably due to internal stress.

Trigonal crystals of the native enzyme could be used for collecting data. We expect that the present quality of the data set obtained from three frames and processed with the CCP4 Laue Software Suite (13384 reflections, 5068 unique, 39% completeness, 3.45 Å resolution) can still be improved.

[1] Z. Ren and K. Moffat, Quantitative Analysis of Synchrotron Laue Diffraction Patterns in Macromolecular Crystallography, *J. Appl. Cryst.* (1995), 28, 461-481.

[2] R.B.G. Ravelli, A.M.F. Hezemans, H. Krabbendam, J. Kroon, Towards Automatic Indexing of the Laue Diffraction Pattern, (accepted for publication in *J. Appl. Cryst.*)

[3] L. Peng, I. Silman, J.L. Sussman and M. Goeldner, Biochemical Evaluation of Photolabile Precursors of Choline and Carbamoylcholine for Potential Time-Resolved Crystallographic Studies on Cholinesterases, *Biochemistry* (submitted).

In Situ X-ray Diffraction Structural Characterization of Hydrogen Uptake in an Operating Nickel-Metal-Hydride Electrode	X27A
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T.R. Thurston, N. Jisrawi, S. Mukerjee, and J. McBreen (BNL)

With the advent of lap top computers, portable video cameras, and especially new regulations promoting electric vehicles, a dramatic increase in demand for battery systems has occurred. There are many conflicting factors that must be satisfied for a battery system to be commercially viable, so it is not surprising that the most promising new battery systems, such as the nickel-metal-hydride system, are underutilized and not well understood.

The metal hydride alloys that have performed best as anodes in battery systems have been based on LaNi_5 or ZrNi_2 prototype alloys, but with the substitution of various other elements such as Ce, Co, Fe, Mn, etc. for portions of the La, Zr, and Ni. A typical example of such an alloy is $\text{Zr}_{0.5}\text{Ti}_{0.5}\text{V}_{0.5}\text{Ni}_{1.1}\text{Mn}_{0.2}\text{Fe}_{0.2}$, which is the alloy we examined here. From a fundamental point of view, it is not understood why the substitution of these various metals improves the hydrogen uptake performance of the alloy. To date, most improvements in nickel-metal-hydride alloy technology have come about through trial and error methods.

In this abstract we demonstrate that it is possible to obtain structural data on such alloys as they charge and discharge hydrogen under in situ electrochemical conditions. With such an approach, information useful for guiding the development of better nickel-metal-hydride alloys can be obtained.

The experiments were performed on X27A with a Si(111) monochromator and LiF(200) analyzer. The x-ray energy was set at 24.5keV, and a transmission scattering geometry was used, so the bulk of the 0.3mm thick electrode was probed. The hard x-ray energy also allowed us to examine the electrode even when it was in a 6 molar KOH electrolyte solution. An electrochemical cell was specially constructed for this experiment, and the electrode was charged and discharged several times while x-ray diffraction experiments were being performed.

The main point of this abstract is that we were able to obtain x-ray diffraction peaks with counting rates up to 30,000/sec under these conditions, and readily monitor the structural state of the bulk of the alloy (not just a few microns within the surface) as hydrogen was electrochemically charged and discharged. The volume change of the unit cell was easily determined as a function of electric potential, and the coexistence of two phases with different hydrogen densities analogous to the gas absorption behavior of this alloy were confirmed. Thus, this work demonstrates that it is possible to routinely monitor the structure of commercially viable nickel-metal-hydride electrodes under in situ electrochemical conditions.

Small Angle X-ray Scattering (SAXS) Investigations of Metal and Semiconductor Nanoscale Size Clusters	X22A, X27A
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T.R. Thurston (BNL), J.P. Wilcoxin, and S. Craft (SNL)

Recently, there has been a dramatic rise in interest in nanoscale size materials. This has occurred largely because new techniques have been developed to manufacture these materials in greater quantities. It has also been recognized that nanoscale size materials often have unique and desirable properties that are different from the corresponding bulk properties. For example, the catalytic properties can become greatly enhanced when a material is reduced to nanoscale dimensions.

Two of the most basic properties that must be characterized when making nanoscale clusters are the average cluster size and the polydispersity of the clusters in a sample. The size can often be roughly estimated from electron microscopy measurements, but the only way to determine both parameters while averaging over the entire sample volume is through small angle x-ray scattering experiments.

To fulfill this characterization need, we have constructed a Bonse-Hart camera which can be mounted at the X22A beam line. Unfortunately, the upstream monochromator crystal of this beam line scatters in a horizontal geometry, so we have had to place a vertically scattering collimator crystal before the sample position. This has usually been a 5-bounce channel cut Si(111) crystal. The analyzer crystal is also a 5-bounce channel cut Si(111) crystal. With this rather simple set up, we have been able to obtain a dynamic range of nearly 10^9 with a range in q from 10^{-4} to $10^0 \text{ \AA}^{-1}$.

The samples we have examined were made using an inverse micelle technique which produces samples with very good polydispersity characteristics. Therefore, the small angle scattering curves show interference effects (wiggles) and it is rather simple to then fit the SAXS data to obtain the size and polydispersity of a sample. We have examined a number of cluster samples including Au, Pd, Rh, and MoS_2 that have been prepared under differing conditions and with different average sizes. More materials will be examined in the future as the inverse micelle technique is developed further.

Synchrotron X-ray Scattering Characterization of High Temperature Superconducting Wires	X27A, X22A
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T.R. Thurston, U. Wildgruber, N. Jisrawi, M. Suenaga, Y.L. Wang (BNL), and P. Halder (IGC)

A CRADA between BNL and Intermagnetics General Corporation was begun in 1995 to use synchrotron x-ray scattering techniques for characterizing $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($T_c=110\text{K}$) 2223 superconducting wires. These wires show commercial promise; for example, higher magnetic field strengths in MRI machines will be attainable using this technology, provided the quality of the wires can be improved.

A major problem in characterizing the wires arises from the fact that the superconducting material is by necessity sheathed in silver cladding. We recognized that the intense x-ray flux available at a synchrotron source allows structural characterizations of these wires which are not possible with any other methods. We mention two of our major conclusions to date here.

We first discuss the differences between early wires made with a single filament of superconducting material compared to more recently made multifilament wires. Generally, the multifilament wires have shown better transport properties than the monofilament wires, but the reason(s) for this improvement have been nebulous. We have found, however, that the full width of the (200) peak of monofilament samples is systematically larger than the full-width of this peak in multifilament samples. Thus, the multifilament samples generally are better textured than the monofilament samples, which improves their transport properties.

In the second example, we consider the phase composition. The starting material for these tapes is 2212 $(\text{Bi,Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ ($T_c=85\text{K}$) phase, along with enough other materials to make 2223 after heat treatments. From analysis of two-theta scans, we have found varying amounts of 2212 in all samples studied to date, with the amount ranging from 4 to 40 percent in nominal 100 percent 2223 samples. Further, by rastering the sample through the x-ray beam, we have shown that the 2212 composition is not homogeneous along the length of all tapes. This data suggests that the phase development process must be examined more closely.

Tail Studies of a Bonse-Hart-Camera *

X27C

J.M.Ablett (Kings College, London, Great Britain), W.A.Caliebe, J.B.Hastings, D.P.Siddons (NSLS)

In order to determine the structure or ordering of samples with spacings in the nano- to micrometer range one has to use softer X-rays or to go to small diffraction angles. The latter can be done by using long flight paths and position sensitive detectors (slit collimation) or by using an analyzer crystal (angular collimation). This idea was proposed and implemented by Bonse and Hart in 1965. Theoretically, these so called Bonse-Hart-cameras should result in very narrow peaks which can be described by a power law, $I \sim \theta^n$, where I is the intensity, θ the deviation of the maximum of the peak and n the number of reflections. To our knowledge this is confirmed experimentally only for a small q -range ($\theta < 10$ arcsec) or for low intensities ($I_{max} \sim 10^5$ photons/s).

The aim of this experiment was to find or to exclude different reasons for the broadening of the peak. For this purpose we built a Bonse-Hart-Camera, using two Si(111) channelcuts, each with 4 reflections and operating at ~ 12 keV ($1\text{\AA}$). The effect of air scattering was eliminated by keeping both crystals in an evacuated tank. The intensity increased due to no absorption by the air, but the peak shape did not change. In order to study the thermal diffuse scattering (TDS), we used three different approaches: we kept the first crystal at room temperature by cooling it, we measured the intensity behind the second crystal with a dispersively mounted second analyser crystal and we mounted a very narrow slit between both crystals in order to eliminate the TDS from the first crystal. All three approaches had no effect on the line shape so that we can only claim that air scattering and TDS are probably not the reasons for the still unexplained broadening.

More experimental and theoretical studies are planned for the next year.

Measurements of the spatial frequency dependent detective quantum efficiency of the FUJI image plate *

X27C

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As part of the mammography project at the NSLS X27C RD beamline, which is described somewhere else in this report, we carried out a number of measurements in order to evaluate the performance of a Fuji image plate detector used together with the Fuji BAS 2000 image plate reader. Typical reading parameters were a sensitivity of 1000, a latitude of 4 and a resolution size of 0.1 mm. The energy of the monochromatic beam was 18 keV. The image plate is a photon integrating pixel detector which can be characterized by the spatial frequency dependent detective quantum efficiency (DQE(f)). Once an image is detected the DQE(f) describes how the input image signal-to-noise ratio is degraded by the detector, taking into consideration the image noise and the spatial resolution. For integrating detectors with a position resolution given by the modulation transfer function (MTF(f)) and the associated image noise defined by the noise power spectrum (NPS(f)) one finds $DQE(f) = DQE(f=0, N) \cdot \|MTF(f)\|^2 / NPS(f)$, with $DQE(f=0, N) = QE / (1 + (\sigma_a^2 / QE \cdot N))$ where QE is the quantum efficiency of the detector, N the average number of incident photons per pixel and σ_a is the intrinsic noise of the detector including read out electronics' noise. The intrinsic noise was measured from an unexposed image plate and a noise equivalent of 3 photons at an energy of 18 keV was found. The QE of the image plate for this energy is approximately 0.98. Plain field images (100 mm · 150 mm), acquired in line scan mode with an approximately 0.5 mm high · 100 mm wide synchrotron beam were used in order to measure the DQE(f=0, N) and the NPS(f). Variations of the flux (from 5 to 5350 photons per pixel) in the plain field were achieved using several plastic absorbers of different thickness. The incident photon number was monitored with an ionization chamber. An image of a sharp edge phantom was used to obtain the edge spread function from which the MTF could be calculated, applying a numerical derivation and a FFT algorithm. Since the signal-to-noise ratio in the image is $SNR_{image} = \sqrt{DQE(f)} \cdot SNR_{poisson}$, details larger than 0.5 mm are transmitted without degradation if the flux is sufficient (≥ 100 photons at that energy) which means that no additional dose is acquired to a patient or phantom in order to achieve the signal-to-noise-ratio given by the poisson statistics. For smaller details, however, one has to increase the dose to achieve the same image quality. At a detail size of 5 LP/mm the DQE(f) drops to zero, which means that no information is transmitted at all (figure 1).

Figure 1. Spatial frequency dependent DQE for $N \geq 100$ photons at 18 keV per pixel

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Monochromatic beam mammography studies with an image plate detector *	X27C
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Preliminary experiments have been carried out at the NSLS X27C beamline to explore potential improvements in breast imaging contrast using monochromatic x-rays. Fuji ST3 PSP image plates read by a model 2000 Fuji reader and standard mammography film were used as detectors. In our present study, images were obtained of an ACR radiology phantom and a Lucite contrast detail phantom at 16, 18, 20, and 22 keV. Phantom thickness varied from 15 to 82 mm. The phantom and the image plate were translated vertically through the stationary fan beam. Exposure to the image plates or film was controlled by the scan rate and various attenuators. The synchrotron images were compared to images obtained with a conventional mammography unit to evaluate improvements in contrast and image quality. The preliminary results show better contrast for the monochromatic beam images with lower absorbed dose in the phantom. The ACR phantom is a standard used to evaluate mammography system performance. It has a set of masses, fibrils, and calcifications embedded in wax. Our images of the ACR phantom scored consistently better than those taken with the standard system.

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PUBLICATIONS

NSLS USERS

Beamline U1A

J.G. Chen, "Selective Activation of C-H and C=C Bonds on Metal Carbides: A Comparison of Reactions of n-Butane and 1,3 Butadiene on Vanadium Carbide Films on V(110)", *J. of Catalysis*, 154, 80, (1995).

J.G. Chen, B.D. DeVries, B. Frühberger, C.M. Kim, and Z.-M. Liu, "Spectroscopic Characterization of Thin Vanadium Carbide Films on a Vanadium (110) Surface: Formation, Stability and Reactivities", Proceedings of the 41st AVS Conference, *J. of Vac.. Sci. and Tech.*, A13, 1600, (1995).

J.G. Chen, C.M. Kim, B. Frühberger, B.D. DeVries, and M.S. Touvelle, "ANEXAFS Determination of the Oxidation State of Vanadium Carbide on V(110): Observation of Charge Transfer from Vanadium to Carbon", *Surf. Sci.*, 321, 145, (1994).

R. Kapoor, S.T. Oyama, B. Frühberger, B.D. DeVries, and J.G. Chen, "Characterization of Early Transition Metal Carbides and Nitrides by NEXAFS", *Catalysis Letters*, 34, 179, (1995).

C.M. Kim, B.D. DeVries, B. Frühberger, and J.G. Chen, "A HREELS and NEXAFS Characterization of Atomic and Molecular Oxygen Species on a Vanadium (110) Surface", *Surf. Sci.*, 327, 81, (1995).

P.J. Lasky, P.H. Lu, M.X. Yang, R.M. Osgood, Jr., B.E. Bent, and P.A. Stevens, "NEXAFS Measurement Indicating a Tilted Molecular Orientation for Methyl Halides on GaAs(110)", *Surf. Sci.*, 336, 140, (1995).

T.J. Lenk, V.M. Hallmark, C.L. Hoffman, J.F. Rabolt, D.G. Castner, C. Erdelen, and H. Ringsdorf, "Structural Investigation of Molecular Organization in Self-Assembled Monolayers of a Semifluorinated Amidethiol", *Langmuir*, 10, 4610-4617, (1994).

M. Xi, M.X. Yang, S.K. Jo, B.E. Bent, and P.A. Stevens, "Benzene Adsorption on Cu(111): Formation of a Stable Bilayer", *J. Chem. Phys.*, 101, 9144, (1994).

Beamline U2B

J.-L. Bantignies, C. Cartier dit Moulin, H. Dexpert, A.-M. Flank, and G.P. Williams, "Asphaltene Adsorption on Kaolinite: Characterization by Infrared Microspectroscopy and X-ray Absorption Spectroscopy", *Compte Rendu del'Acad. Sci. Paris*, 320, 699, (1995).

R. Biscardi, G. Ramirez, and G.P. Williams, "Effects of RF Side-Bands on Spectral Reproducibility For Infrared Synchrotron Radiation", *Rev. Sci. Instrum.*, 66, 1856, (1995).

G.L. Carr, M. Hanfland, and G.P. Williams, "The Mid-Infrared Beamline at the NSLS Port U2B", *Rev. Sci. Instrum.*, 66, 1643, (1995).

G.L. Carr, J. Reffner, and G.P. Williams, "Performance of an Infrared Microspectrometer at the NSLS", *Rev. Sci. Instrum.*, 66, 1490, (1995).

R.J. Hemley, and H.K. Mao, "Progress on Hydrogen at Ultrahigh Pressures", in Elementary Processes in Dense Plasmas, edited by S. Ichimaru, and S. Ogata, Addison-Wesley, Reading, Mass., pp. 269-280, (1995).

R.J. Hemley, H.K. Mao, T.S. Duffy, J.H. Eggert, A.F. Goncharov, M. Hanfland, M. Li, M. Somayazulu, W. Vos, and C.S. Zha, "Dense Hydrogen on The Outer Solar System: Implications from Recent High-Pressure Experiments", in Deep Earth and Planetary Volatiles, edited by K. Farley, American Institute of Physics, College Park, MD, pp. 250-260, (1995).

R.J. Hemley, Z.G. Soos, M. Hanfland, and H.-k. Mao, "Charge Transfer States in Dense Hydrogen", *Nature*, 369, 384, (1994).

J.A. Reffner, P.A. Martoglio, and G.P. Williams, "FT-IR Microscopical Analysis With Synchrotron Radiation: The Microscope Optics and System Performance", *Rev. Sci. Instrum.*, 66, 1298, (1995).

D.L. Wetzel, "Microbeam Molecular Spectroscopy of Biological Materials", in Food Flavors: Generation, Analysis, and Process Influence, edited by G. Charalambous, Elsevier, p. 2039, (1995).

Beamline U3C

D.R. Mullins, and P.F. Lyman, "Enhancement of Selective Decomposition: Methanethiol on C Covered W(001)", *J. Phys. Chem.*, 99, 5548, (1995).

Beamline U4A

K. Breuer, D.M. Goldberg, K.E. Smith, M. Greenblatt, and W. McCarroll, "Resonant Photoemission Study of the Electronic Structure of $K_{0.3}MoO_3$ ", *Solid State Comm.*, 94, 601, (1995).

U. Diebold, H.-S. Tao, N.D. Shinn, and T.E. Madey, "Electronic Structure of Ultrathin Fe Films on $TiO_2(110)$ Studied with Soft-x-ray Photoelectron Spectroscopy and Resonant Photoemission", *Phys. Rev.*, B50, 14474, (1994).

Y. Wu, H.-S. Tao, E. Garfunkel, T.E. Madey, and N.D. Shinn, "Growth, Interfacial Alloying, and Oxidation of UltraThin Al Films on Ru(0001)", *Surf. Sci.*, 336, 123, (1995).

Beamline U4B

V. Chakarian, Y.U. Idzerda, G. Meigs, E.E. Chaban, J.-H. Park, and C.T. Chen, "Element-Specific Vector Magnetometry With Magnetic Circular Dichroism", *Appl. Phys. Lett.*, **66**, 3368, (1995).

V. Chakarian, Y. U. Idzerda, G. Meigs, and C. T. Chen, "Applications of Soft X-ray Magnetic Circular Dichroism", *IEEE Trans. Magn.*, **31**, 3307, (1995).

V. Chakarian, H.-J. Lin, Y. U. Idzerda, E. E. Chaban, G. Meigs, J.-H. Park, C. J. Gutierrez, G. A. Prinz, and C. T. Chen, "Element-Specific Vector Magnetometry (ESVM) via Soft X-ray Magnetic Circular Dichroism", *Mater. Res. Soc. Symp. Proc.*, **375**, (1995).

J. Chen, J. Christiansen, S.J. George, J. van Elp, R. Tittsworth, B.J. Hales, S. Al-Ahmad, D. Coucouvanis, N. Campobasso, J.T. Bolin, and S.P. Cramer, "Extended X-ray Absorption Fine Structure and L-Edge Spectroscopy of Nitrogenase Molybdenum-Iron Protein", *Molybdenum Enzymes, Cofactors, and Model Systems*, edited by I. Stiefel, D. Coucouvanis, and W.E. Newton, ACS Symposium Series, p. 535, (1994).

O.C. Mullins, S. Mitra-Kirkley, J. van Elp, and S.P. Cramer, "Molecular Structure of Nitrogen in Coal from XANES Spectroscopy", *Applied Spectroscopy*, **47**, 1268-1275, (1993).

G. Peng, J. van Elp, H. Jang, L. Que, Jr., W.H. Armstrong, and S.P. Cramer, "L-Edge X-ray Absorption and X-ray Magnetic Circular Dichroism of Oxygen-Bridged Di-nuclear Iron Complexes", *J. Am. Chem. Soc.*, **117**, 2515-2519, (1995).

L. Sève, J.M. Tonnerre, D. Raoux, J.F. Bobo, M. Piechuh, M. DeSantis, P. Troussel, J.M. Brot, V. Chakarian, C.-C. Kao, and C.T. Chen, "Resonant Magnetic Scattering in Soft X-ray Range Using Multilayers", *J. Magn. Magn. Mater.*, **148**, 68, (1995).

J.M. Tonnerre, L. Sève, D. Raoux, B. Rodmacq, M. DeSantis, P. Troussel, J.M. Brot, V. Chakarian, C.-C. Kao, E.D. Johnson, and C.T. Chen, "X-Ray Resonant Magnetic Scattering at L-Edges of 3d Transition Metals using Multilayers", *Proceeding of the First European Synchrotron Radiation Conference, Nucl. Instrum. And Meth. In Phys. Rev.*, **B97**, 444, (1995).

J. van Elp, G. Peng, B.G. Searle, S. Mitra-Kirtley, Y.-H. Huang, M.K. Johnson, Z.H. Zhou, M.W.W. Adams, M.J. Maroney, and S.P. Cramer, "Electronic Structure and Symmetry in Nickel L Edge X-ray Absorption Spectroscopy: Application to a Nickel Protein", *J. Am. Chem. Soc.*, **116**, 1918-1923, (1994).

J. van Elp, G. Peng, Z.H. Zhou, M.W.W. Adams, N. Baidya, P.K. Mascharak, and S.P. Cramer, "Nickel L-Edge X-ray Absorption Spectroscopy of Pyrococcus Furiosus Hydrogenase", *Inorg. Chem.*, **34**, 2501-2504, (1995).

J. van Elp, S.J. George, G. Peng, B.G. Searle, Z.H. Zhou, M.W.W. Adams, C.T. Chen, and S.P. Cramer, "Soft X-ray Magnetic Circular Dichroism on a Paramagnetic Bioinorganic System", *X-ray and Ultraviolet Polarimetry*, edited by S. Fineschi, *SPIE*, **2010**, 181, (1993).

Beamline U4IR

C.J. Hirschmugl and G.P. Williams, "Signal to Noise Improvements with a New Far-IR Rapid-Scan Michelson Interferometer", *Rev. Sci. Instrum.*, **66**, 1487, (1995).

C.L.A. Lamont, B.N.J. Persson, and G.P. Williams, "Dynamics of Atomic Adsorbates: Hydrogen on Cu(111)", *Chem. Phys. Letts.*, **243**, 249, (1995).

K. Lin, R. Tobin, and P. Dumas, "Adsorbate-Induced Changes in the Broadband IR Reflectance of a Metal: Oxygen on Cu(100)", *Phys. Rev.*, **B49**, 17273, (1994).

K. Lin, R. Tobin, and P. Dumas, "Infrared Spectroscopy of Formate on Oxygen Predosed Cu(100): Broadband Reflectance and Low Frequency Vibrations", *J. Vac. Sci. & Tech.*, **13**, 1579, (1995).

M.C. Martin, X. Du, and L. Mihaly, "Infrared Studies of Single Crystal C60: Silent and Higher Order Vibrational Modes", Proceedings of the 1994 International Winterschool on Electronic Properties of Novel Materials: Progress in Fullerenes Research, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth, World Scientific Publishing Co., p. 353, (1994).

C.A. Melendres, B. Beden, and G.A. Bowmaker, "Far Infrared Spectroscopy of a Platinum Electrode *in situ* Using a Synchrotron Source", *J. Electroanal Chem.*, **383**, 191, (1995).

Beamline U5U

N. Brookes, Y. Chang, and P.D. Johnson, "The Ag/Fe(001) Interface", *Phys. Rev.*, **B50**, 15330-15336, (1994).

P.D. Johnson, "Spin Polarized Photoemission Studies of Magnetic Quantum Well States", *J. Magn. Magn. Mat.*, **148**, 167-171, (1995).

D. Li, J. Mattson, J. Pearson, S.D. Bader, and P.D. Johnson, "Photoemission Study of Quantum Confinement by a Finite Barrier; Cu/Co(wedge)/Cu(100)", *Phys. Rev.*, **B51**, 7195-7199, (1995).

D. Li, J. Pearson, S.D. Bader, D.N. McIlroy, C. Waldfried, and P.A. Dowben, "Spin Polarized Photoemission Studies of the Exchange Splitting of the Gd 5d Electrons Near the Curie Temperature", *Phys. Rev.*, **B51**, 13895-13898, (1995).

B. Sinkovic, P.D. Johnson, N.B. Brookes, A. Clarke, and N.V. Smith, "A Spin Polarized Auger Electron Diffraction Study of the Magnetic Poisoning of Fe(001) by Sulfur", *Phys. Rev.*, **B52**, R6955-6958, (1995)

Beamline U8B

M. M. Banaszak Holl, S. Lee, and F. R. McFeely, "Core Level Photoemission and the Structure of the Si/SiO₂ Interface: a Reappraisal.", *Appl. Phys. Lett.*, **65**, 1097 (1994).

M. M. Banaszak Holl, and F. R. McFeely, "The Si/SiO₂ Interface: New Structures and Well-Defined Model Systems.", *Phys. Rev. Lett.*, **71**, 2441, (1994).

S. Lee, S. Makan, M. M. Banaszak Holl, and F. R. McFeely, "Synthetic Control of Solid/Solid Interfaces: Analysis of Three New Silicon/Silicon Oxide Interfaces by Soft X-ray Photoemission.", *J. Am. Chem. Soc.*, 116, 11819, (1994).

Beamline U11

T.J. Buckley, R.D. Johnson, III, R.E. Huio, Z. Zhang, S.-C. Kuo, and R.B. Klemm, "Ionization Energies, Appearance Energies and Thermochemistry of CF_2O and FCO ", *J. Phys. Chem.*, 99, 4879, (1995).

B.A. McDougall, T. Balasubramanian, and E. Jensen, "Phonon Contribution to Quasiparticle Lifetimes in Cu Measured by Angle-Resolved Photoemission", *Phys. Rev.*, B51, 13891, (1995).

P.S. Monks, L. J. Stief, M. Krauss, S.C. Kuo, Z. Zhang, and R.B. Klemm, "A Discharge Flow-Photoionization Mass Spectrometric Study of the $\text{NO}_3(2A_2')$ Radical: Photoionization Spectrum, Adiabatic Ionization Energy and Ground State Symmetry", *J. Phys. Chem.*, 98, 10017, (1994).

L.J. Stief, F.L. Nesbitt, W.A. Payne, S.-C. Kuo, W. Tao, and R.B. Klemm, "Rate Constant and Reaction Channels for the Reaction of Atomic Nitrogen with the Ethyl Radical", *J. Chem. Phys.*, 102, 5309, (1995).

A.J. Yench, A. Hopkirk, J.R. Grover, B.-M. Cheng, H. Lefebvre-Brion, and F. Keller, "Ion-Pair Formation in the Photodissociation of HF and DF", *J. Chem. Phys.*, 103, 2882, (1995).

Z. Zhang, S.-C. Kuo, R.B. Klemm, P.S. Monks, and L.J. Stief, "A Discharge Flow-Photoionization Mass Spectrometric Study of the $\text{FO}(X^2\Pi_i)$ Radical: Photoionization Efficiency Spectrum and Ionization Energy", *Chem. Phys. Lett.*, 229, 377, (1994).

Beamline U12B

P.F. Lyman, and D.R. Mullins, "Structural Rearrangements in the C/W(100) Surface System", *Phys. Rev.*, B51, 13623, (1995).

Beamline U13UA

C.J. Buckley, S.J. Bellamy, X. Zhang, G. Dermody, and S. Hulbert, "The NEXAFS of Biological Calcium Phosphates", *Rev. Sci. Instrum.*, 66, 1322, (1995).

G.S. Dermody, The Development of a Transmission X-ray Flux Monitor for an Undulator Beamline on a Vacuum Ultraviolet Synchrotron Storage Ring, Master of Science, London University, (1995).

K. Lee, S. L. Hulbert, P. Kuiper, D. Ji, and D. M. Hanson, "Auger, Zero-Energy Photo-Electron, Coincidence Spectroscopy (AZEPECO): Chemical-Site-Selective Auger Electron Spectroscopy", *Nucl. Instrum. Methods*, A347, 446, (1994).

D.R. Mullins, D.R. Huntley, and S.H. Overbury, "The Nature of the Sulfur-Induced Reconstruction on Ni(111)", *Surf. Sci.*, 323, L287, (1995).

T.S. Rufael, D.R. Huntley, D.R. Mullins, and J.L. Gland, "Adsorption and Reactions of Benzenethiol on the Ni(111) Surface", *J. Phys. Chem.*, **98**, 13022, (1994).

T.S. Rufael, D.R. Mullins, J.L. Gland, and D.R. Huntley, "Methyl Thiolate on Ni(111): Multiple Adsorption Sites and Mechanistic Implications", *J. Phys. Chem.*, **99**, 11472, (1995).

E.E. Shekel, Spin Polarized Photoelectron Spectroscopy in the Soft X-ray Regime, PhD., New York University, January, (1995).

B. Sinkovic, E. Shekel, and S. L. Hulbert, "Spin-Resolved Iron Surface Density of States", *Phys. Rev.*, **B52**, R8696, (1995).

K. E. Smith, K. Breuer, D. Goldberg, M. Greenblatt, W. McCarroll, and S. L. Hulbert, "Defects in Quasi-One Dimensional Oxide Conductors: $K_{0.3}MoO_3$ ", *Mat. Res. Soc. Symp. Proc.*, **375**, 133, (1995).

C. Woodbridge, Electronic Decay and Subsequent Fragmentation of Methane Induced by Soft X-rays, PhD., University at Stony Brook, December, (1995).

Beamline U13UB

B. LaFontaine, A.A. MacDowell, Z. Tan, G.N. Taylor, D.L. White, D.M. Tennant, and O.R. Wood II, "Real-Time, Sub-Micron Fluorescence Imaging of Extreme Ultraviolet Aerial Images", OSA Proceedings on Extreme Ultraviolet Lithography, edited by F. Zernike and D.T. Attwood, Optical Society of America, Washington, DC, Vol. 23, pp.177-181, (1994).

B. LaFontaine, A.A. MacDowell, Z. Tan, D.L. White, G.N. Taylor, J.E. Bjorkholm, D.M. Tennant, and S. Hulbert, "SubMicron, Soft X-ray Fluorescence Imaging", *Appl. Phys. Lett.*, **66**, 282-284, (1995).

B. LaFontaine, D. L. White, A. A. MacDowell, Z. Tan, D. M. Tennant, and O.R. Wood II, "Extreme Ultraviolet Moire Interferometry", OSA Proceedings on Extreme Ultraviolet Lithography, edited by F. Zernike and D.T. Attwood, Optical Society of America, Washington, DC, Vol. 23, pp.167-170, (1994).

B. LaFontaine, D.L. White, O.R. Wood II, A.A. MacDowell, Z. Tan, G.N. Taylor, D.M. Tennant, and S. Hulbert, "Real Time Observation of Extreme Ultra-Violet Aerial Images by Fluorescence Micro-Imaging", *J. Vac. Sci. Technol.*, **B12**, 3576-3579, (1994).

B.M. Lum, A.R. Neureuther, B. LaFontaine, A.A. MacDowell and O.R. Wood II, "Validation of Modeling Hoechst AZ PN114 for EUV Projection Lithography and Investigation of Diffusion Effects", OSA Proceedings on Extreme Ultraviolet Lithography, edited by F. Zernike and D.T. Attwood, Optical Society of America, Washington, DC, Vol. 23, pp.184-192, (1994).

A. MacDowell, "Extreme Ultraviolet Lithography at the NSLS", *Synch. Rad. News*, **7**, 14-17, (1994).

Z. Tan, A.A. MacDowell, B. LaFontaine, J.E. Bjorkholm, R.R. Freeman, M.D. Himel, D.M. Tennant, D. Taylor, O.R. Wood II, W.K. Waskiewicz, D.L. Windt, and D.L. White, "At-Wavelength Metrology of 13nm Lithography Imaging Optics", *Rev. Sci. Instrum.*, **66**, 2241-2247, (1995).

Z. Tan, A.A. MacDowell, B. LaFontaine, J. Russo, J. Bjorkholm, D.M. Tennant, D.W. Taylor, M.D. Himel, O.R. Wood II, R.R. Freeman, W.K. Waskiewicz, D.L. White, S. Spector, A. Ray-Chaudhuri, and R.H. Stulen, "At-Wavelength Metrology of EUVL Cameras Using Lateral-Shearing Interferometry", OSA Proceedings on Extreme Ultraviolet Lithography, edited by F. Zernike and D.T. Attwood, Optical Society of America, Washington, DC, Vol. 23, pp. 151160, (1994).

G.N. Taylor, R.S. Hutton, S.M. Stein, C.H. Boyce, O.R. Wood II, B. LaFontaine, A.A. MacDowell, D.R. Wheeler, G.D. Kubiak, A.K. Ray-Chaudhuri, K. Berger, and D. Tichenor, "Extreme UV Resist Technology: the Limits of Silylated Resist Resolution", *SPIE*, **2437**, 308, (1995).

G.N. Taylor, R.S. Hutton, S.M. Stein, C.H. Boyce, B. LaFontaine, A.A. MacDowell, D.R. Wheeler, and O.R. Wood II, "Limitations to Silylated Resist Technology", OSA Proceedings on Extreme Ultraviolet Lithography, edited by F. Zernike and D.T. Attwood, Optical Society of America, Washington, DC, Vol. 23, pp.182-183, (1994).

D.L. White, O.R. Wood II, S. Spector, A.A. MacDowell, and B. LaFontaine, "Modification of the Coherence of Undulator Radiation", *Rev. Sci. Instrum.*, **66**, 1930-1933, (1995).

O.R. Wood II, J.E. Bjorkholm, K.F. Dreyer, L.E. Fetter, M.D. Himel, R.R. Freeman, D.M. Tennant, J.E. Griffith, G.N. Taylor, W.K. Waskiewicz, D.L. White, D.L. Windt, A.A. MacDowell, B. LaFontaine, B. Lum, A.R. Neureuther, J.B. Kortright, E.K. Gullikson, and K.B. Nguyen, "Experiments and Simulations of EUV Lithographic Resist Patterning at Wavelengths From 7 to 40 nm", OSA Proceedings on Extreme Ultraviolet Lithography, edited by F. Zernike and D.T. Attwood, Optical Society of America, Washington, DC, Vol. 23, pp.83-88, (1994).

O.R. Wood II, J.E. Bjorkholm, L. Fetter, M.D. Himel, A.A. MacDowell, D.M. Tennant, B. LaFontaine, J.E. Griffith, G.N. Taylor, W.K. Waskiewicz, D.L. Windt, J.B. Kortright, E.K. Gullikson, and K. Nguyen, "Wavelength Dependence of Resist Sidewall Angle in Extreme Ultraviolet Lithography", *J. Vac. Sci. Technol.*, **B12**, 3841-3845, (1994).

Beamline U14A

Z.M. Stadnik, G.W. Zhang, A.-P. Tsai, and A. Inoue, "Electronic Structure of Decagonal $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ and $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$ ", *Phys. Rev.*, **B51**, 11358, (1995).

Z.M. Stadnik, G.W. Zhang, A.-P. Tsai, and A. Inoue, "Electronic Structure of Icosahedral $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ Studied by Photoemission Spectroscopy", *Phys. Rev.*, **B51**, 4023, (1995).

Z.M. Stadnik, G.W. Zhang, A.-P. Tsai, and A. Inoue, "Are Decagonal Quasicrystals the Hume-Rothery Phases?", *Phys. Lett.*, **A198**, 237, (1995).

Z.M. Stadnik, G.W. Zhang, A.-P. Tsai, and A. Inoue, "Photoemission Studies of Stable, Icosahedral Alloys", Aperiodic '94, Proceedings of the International Conference on Aperiodic Crystals, edited by G. Chapuis and W. Paciorek, World Scientific, Singapore, p. 249, (1995).

Z.M. Stadnik, G.W. Zhang, A.-P. Tsai, and A. Inoue, "Synchrotron-Radiation Studies of Valence Bands in Stable, Decagonal $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ and $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$ ", Aperiodic '94 Proceedings of the International Conference on Aperiodic Crystals, edited G. Chapuis and W. Paciorek, World Scientific, Singapore, p. 254, (1995).

G.W. Zhang, Z.M. Stadnik, A.-P. Tsai, A. Inoue, and T. Miyazaki, "Electronic Structure of Icosahedral Alloys: The Case of $\text{Al}_{65}\text{Cu}_{20}\text{Os}_{15}$ ", *Z Phys.*, B97, 439, (1995).

Beamline X1A

- H. Ade, A.P. Smith, S. Cameron, R. Cieslinski, G. Mitchell, B. Hsiao, and E. Rightor, "X-ray Microscopy in Polymer Science: Prospects of a "New" Imaging Technique", *Polymer*, 36, 1843-1848, (1995).
- C.J. Buckley, S.J. Bellamy, X. Zhang, G. Dermody, and S. Hulbert, "The NEXAFS of Biological Calcium Phosphates", *Rev. Sci. Instrum.*, 66, 1322-1324, (1995).
- H.N. Chapman, C. Jacobsen, and S. Williams, "Applications of a CCD Detector in a Scanning Transmission X-ray Microscope", *Rev. Sci. Instrum.*, 66, 1332-1334, (1995).
- G.D. Cody, R.E. Botto, H. Ade, S. Behal, M. Disko, and S. Wirick, "C-NEXAFS Microanalysis and Scanning X-ray Microscopy of Microheterogeneities in a High-Volatile A Bituminous Coal", *Energy & Fuels*, 9, 75-83, (1995).
- G.D. Cody, R.E. Botto, H. Ade, S. Behal, M. Disko, and S. Wirick, "Inner-Shell Spectroscopy and Imaging of a Subbituminous Coal: *in situ* Analysis of Organic and Inorganic Microstructure Using C(1s), Ca(2p), and Cl(2s) NEXAFS", *Energy & Fuels*, 9, 525-533, (1995).
- L. Haddad, "Demonstration of Ultra High Resolution Soft X-ray Tomography Workshop on Scientific Applications of Coherent X-rays", *SLAC Report*, edited by J. Arthur, G. Matterlik, and H. Winick, Stanford, CA: SLAC, 437, pp. 179-191, (1994).
- W.S. Haddad, I. McNulty, J.E. Trebes, E.H. Anderson, R.A. Levesque, and L. Yang, "Ultrahigh Resolution X-ray Tomography", *Science*, 266, 1213-1215, (1994).
- J. Kirz, C. Jacobsen, and M. Howells, "Soft X-ray Microscopes and Their Biological Applications", *Quarterly Reviews of Biophysics*, 28, 33-130, (1995).
- C.-H. Ko, J. Kirz, H. Ade, S. Hulbert, E. Johnson, and E. Anderson, "Applications of the X1A Scanning Photoemission Spectromicroscope for Element Identification on Material Surfaces", *Mat. Res. Soc. Symp. Proc.*, 375, 303-305, (1995).
- C.-H. Ko, J. Kirz, H. Ade, E. Johnson, S. Hulbert, and E. Anderson, "Development of a Second Generation Scanning Photoemission Microscope with a Zone Plate Generated Microprobe at the National Synchrotron Light Source", *Rev. Sci. Instrum.*, 66, 1416-1418, (1995).
- I. McNulty, W.S. Haddad, J.E. Trebes, and E.H. Anderson, "Soft X-ray Scanning Microtomography with Submicrometer Resolution", *Rev. Sci. Instrum.*, 66, 1431-1433, (1995).
- D. Sayre, and H.N. Chapman, "X-ray Microscopy", *Acta Cryst.*, A51, 237-252, (1995).
- S. Williams, C. Jacobsen, J. Kirz, J. Maser, S. Wirick, X. Zhang, H. Ade, and M. Rivers, "Instrumentation Developments in Scanning Soft X-ray Microscopy at the NSLS", *Rev. Sci. Instrum.*, 66, 1271-1275, (1995).
- X. Zhang, C. Jacobsen, S. Lindaas, and S. Williams, "Exposure Strategies for PMMA From *in situ* XANES Spectroscopy", *J. Vac. Sci. Technol.*, B13, 1477-1483, (1995).
- X. Zhang, H. Ade, C. Jacobsen, J. Kirz, S. Lindaas, S. Williams, and S. Wirick, "Micro-XANES: Chemical Contrast in the Scanning Transmission X-ray Microscope", *Nucl. Instrum. Meth.*, A347, 431-435, (1994).

Beamline X1B

W. Eberhardt, "Spectroscopy and Dynamics of the Electronic Decay of Core Electron Excitations in Isolated and Chemisorbed Molecules", In Application of Synchrotron Radiation to High Resolution Studies of Molecules and Molecular Adsorbates on Surfaces, edited by W. Eberhardt, *Springer Series in Surface Science*, 35, 203, (1995).

S. Eisebitt, J.E. Rubensson, M. Nicodemus, T. Böske, S. Blügel, W. Eberhardt, K. Radcrmacher, WS. Mantl, and G. Bihl mayer, "Electronic Structure of Buried α -FeSi₂ and β -FeSi₂ Layers: Soft X-ray Emission and Absorption Studies Compared to Band-Structure Calculations", *Phys. Rev.*, B50, 18330-18340, (1994).

B.S. Itchkawitz, B. Kempgens, H.M. Köppe, J. Feldhaus, A.M. Bradshaw, and W.B. Peatman, "Absolute Photoabsorption Cross-Section Measurements of Simple Molecules in the Core-Level Region", *Rev. Sci. Instrum.*, 66, 1531, (1995).

H.M. Köppe, A.L.D. Kilcoyne, J. Feldhaus, and A.M. Bradshaw, "Photon Energy Dependence of the Vibrational Fine Structure in Core Level Photoemission Spectra Near Threshold", *J. Chin. Chem. Soc.*, 42, 255, (1995).

J. Lüning, J.E. Rubensson, S. Eisebitt, and W. Eberhardt, "Selectively Excited Core-to-core Fluorescence of Potassium Halides", *Phys. Rev.*, B51, 10399-10405, (1995).

M. Neeb, A. Kivimäki, B. Kempgens, H.M. Köppe, and A.M. Bradshaw, "Conjugate Shake-up-enhanced Auger Transitions in N₂", *Phys. Rev.*, A52, 1224, (1995).

Z. Xu, Y. Liu, P.D. Johnson, B. Itchkawitz, K. Randall, J. Feldhaus, and A. Bradshaw, "A Spin Polarized Photoemission Study of the Fe 3s Multiplet", *Phys. Rev.*, B51, 7912-7915, (1995).

Beamline X3A1

R. Bolotovskiy, A. Darovsky, V. Kezerashvili, and P. Coppens, "The Use of Imaging Plates in Electron Density Mapping with Synchrotron X-rays", *J. Synch. Rad.*, 2, 181, (1995).

R. Bolotovskiy, M.A. White, A. Darovsky, and P. Coppens, "The "Seed-Skewness" Method for Integration of Peaks on Imaging Plates", *J. Appl. Cryst.*, 28, 86, (1995).

B. Chu, F. Yeh, Y. Li, P.J. Harney, J. Rousseau, A. Darovsky, and D.P. Siddons, "Construction of a High-Energy Bonse-Hart Ultrasmall-angle X-ray Scattering Instrument", *Rev. Sci. Instrum.*, 65, 3233, (1994).

B. Chu, Q.C. Ying, F.-J. Yeh, A. Patkowski, W. Steffen, and E.W. Fischer, "An X-ray Photon Correlation Experiment", *Langmuir*, 11, 1419 (1995).

A. Darovsky, R. Bolotovskiy, and P. Coppens, "An Anti-Scatter Device for Low Temperature Crystallographic Experiments with Imaging Plates", *J. Appl. Cryst.*, 27, 1039, (1994).

A. Darovsky, V. Kezerashvili, R. Harlow, and I. Mutikainen, "Structure of Oxidized Forms of Neodymium and Praseodymium (Bis)phthalocyanines", *Acta Cryst.*, B50, 582, (1994).

A. Darovsky, I. Meshkovskiy, and P. Coppens, "A Multi-Wavelength Monochromator for the X3A1 Fixed-Angle Station at the National Synchrotron Light Source", *J. Synch. Rad.*, 2, 77, (1995).

A. Darovsky, I. Meshkovskiy, and P. Coppens, "Compact Monochromator for the Multipurpose X3 Synchrotron Beamline at NSLS", *Rev. of Sci. Instrum.*, 66/2, 2085, (1995).

K. Tan, Y. Ko, A. Darovsky, and J.B. Parise, "The Synthesis of a Novel Open Framework Sulfide, $\text{CuGe}_2\text{S}_5 \cdot (\text{C}_2\text{H}_5)_4\text{N}$ and its Structure Solution using Synchrotron Imaging Plate Data", *J. Am. Chem. Soc.*, 117, 7039, (1995).

Beamline X3A2

S. Z. D. Cheng, S. W. Lee, E. Von Meerwall, and B. S. Hsiao, "RMolecular Shape Effects on the Crystallization, Melting and Morphology of Star Poly(ethylene oxide) Fractions", *ACS Polym. Prep.*, 36/1, 259, (1995).

Y.W. Cheung, R.S. Stein, B. Chu, and G. Wu, "Evolution of Crystalline Structures of Poly(epsilon-caprolactone) (PCL)/Polycarbonate (PC) Blends. 1. Isothermal Crystallization Kinetics as Probed by Synchrotron Small-Angle X-ray Scattering", *Macromolecules*, 27, 3589, (1994).

M. deBoissieu, P. Stephens, M. Boudard, C. Janot, D.L. Chapman, and M. Audier, "Anomalous X-ray Diffraction Study of the AlPdMn Icosahedral Phase", *J. Phys. Condens. Mat.*, 6, 10725, (1994).

P. Harney, B. S. Hsiao, A. D. Kennedy, and B. Chu, "Synchrotron SAXS Studies of Glassy PET Fiber During Deformation", *ACS Polym. Prep.*, 36/1, 308, (1995).

B. S. Hsiao, B. B. Sauer, R. A. Leach, B. Chu, P. Harney, H. G. Zachman, and S. Seifert, "New Insight of Isothermal Melt Crystallization Via Time-Resolved Simultaneous SAXS/WAXD Measurements", *ACS Polym. Prep.*, 36/1, 342, (1995).

B. S. Hsiao, B. B. Sauer, R. Verma, B. Chu, P. Harney, H. G. Zachman, and S. Seifert, "New Insight of Isothermal Melt Crystallization Via Time-Resolved Simultaneous SAXS/WAXD Measurements", *Macromolecules*, 28, 6931-6936, (1995).

X. Lu, W. P. Stechle, Jr., B. Hsiao, and R. A. Weiss, "Thermally Induced Microstructure Transitions in a Block Copolymer Ionomer", *Macromolecules*, 28, 2831-2839, (1995).

B. B. Sauer, and B. S. Hsiao, "Effect of Heterogeneous Distribution of Lamellar Stacks on Amorphous Relaxations in Semicrystalline Polymers", *Polymer*, 36/1, 2553-2558, (1995).

A. Spijkerman, A. Meetsma, J.L. de Boer, Y. Gao, and S. van Smaalen, "Modulated Structure of NiTa_2Se_7 in its Incommensurate Charge-Density-Wave State at 16K", *Phys. Rev.*, B52, 3892, (1995).

M. Takenaka, K. Linliu, Q. Ying, B. Chu, and D. Peiffer, "Synchrotron Small Angle X-ray Scattering of Slow Spinodal Decomposition in a Block Copolymer", *Macromolecules*, 28, 2700, (1995).

R. Verma, A. Biswas, and B. S. Hsiao, "Small Angle X-Ray Scattering for Lamellar Semi-Crystalline Systems: Some Novel Data Analysis Techniques", *ACS Polym. Prep.*, 36/1, 348, (1995).

R. Verma, B. Chu, B. S. Hsiao, and H. Marand, "Real Time SAXS Studies of Lamellar Level Morphological Development in PEEK", *ACS Polym. Prep.*, 36/1, 346, (1995).

G. Wu, B. Chu, and D.K. Schneider, "SANS Study of Micellar Structure of PEO-PPO-PEO Aqueous Solution", *J. Phys. Chem.*, 99, 5094, (1995).

G. Wu, B. Chu, and D.K. Schneider, "Small-angle Neutron Scattering Study of Polymeric Micellar Structures", *J. Phys. Chem.*, 98, 12018, (1995).

Beamline X3B1

- T. Ami, M.K. Crawford, R.L. Harlow, Z. Wang, D.C. Johnston, Q. Huang, and R.C. Erwin, "Magnetic Susceptibility and Low Temperature Structure of the Linear Chain Cuprate Sr_2CuO_3 ", *Phys. Rev.*, B51, 5994, (1995).
- M.K. Crawford, R.L. Harlow, E.M. McCarron, D.E. Cox, and Q. Huang, "Effects of Structural Phase Transitions on Superconductivity and Magnetism in Substituted Derivatives of La_2CuO_4 ", *Physica C*, 235-240, 170, (1994).
- M.K. Crawford, R.L. Harlow, E.M. McCarron, N. Herron, W.E. Farneth, W. Donahue, B.A. Parkinson, and J. Schirber, "Synchrotron X-ray Powder Diffraction Study of Electrochemically Oxidized $\text{La}_2\text{CuO}_{4+\delta}$ and $\text{La}_{2-x}\text{Nd}_x\text{CuO}_{4+\delta}$ ", *J. Phys. Chem. Solids*, 56, 1459, (1995).
- A. Darosky, L. Meshkovsky, and P. Coppens, "Compact Monochromator for the Multipurpose X3 Synchrotron Beamline at NSLS", *Rev. Sci. Instrum.*, 66/2, 2085, (1995).
- R.E. Dinnebier, P.W. Stephens, J.K. Carter, A.N. Lommen, P.A. Heiney, A.R. McGhie, L. Brard, and A.B. Smith III, "X-ray Powder Diffraction Structure of Triclinic $\text{C}_{60}\text{Br}_{24}(\text{Br}_2)_2$ ", *J. Appl. Crystall.*, 28, 327, (1995).
- N. Herron, D.L. Thorn, and R.L. Harlow, "Molecular Precursors to Functional Materials", Molecular Designed Ultrafine/Nanostructured Materials, edited by K. E. Gonsalves, *MRS Symp. Proc.*, 351, (1994).
- N. Herron, D.L. Thorn, R.L. Harlow, G.A. Jones, J.B. Parise, J.A. Fernandez-Baca, and T. Vogt, "The Preparation and Structural Characterization of Two New Phases of Aluminum Trifluoride", *Chem. Of Mater.*, 7, 75, (1995).
- D. Koller, M.C. Martin, P.W. Stephens, L. Mihály, S. Pekker, A. Jánossy, O. Chauvet, and L. Forró, "Polymeric Alkali Fullerides are Stable in Air", *Appl. Phys. Letts.*, 66, 1015, (1994).
- A.R. McGhie, J.E. Fischer, P.W. Stephens, R.L. Cappelletti, D.A. Neumann, W.H. Mueller, H. Mohn, and H.U. ter Meer, "Phase Transitions in Solid C70: Supercooling, Metastable Phases and Impurity Effect", *Phys. Rev.*, B49, 12614, (1994).
- Z.H. Ming, S. Huang, Y.L. Soo, Y.H. Kao, T. Carns, and K.L. Wang, "Interfacial Roughness Scaling and Strain in Lattice Mismatched $\text{Si}_{0.4}\text{Ge}_{0.6}$ Thin Films on Si", *Appl. Phys. Lett.*, 67, 629, (1995).
- Z.H. Ming, Y.L. Soo, S. Huang, Y.H. Kao, K. Stair, G. Devane, and C. Choi-Feng, "Thickness Modulation of InGaAs/GaAs Superlattice Studied by Large Angle X-ray Scattering", *Appl. Phys. Lett.*, 66, 165, (1994).
- Z.H. Ming, Y.L. Soo, S. Huang, Y.H. Kao, K. Stair, G. Devane, and C. Choi-Feng, "X-ray Scattering Studies of Interfacial Microstructures in $\text{In}_x\text{Ga}_{1-x}\text{As}$ /GaAs Superlattices", *Mat. Res. Soc. Symp. Proc.*, 375, 171, (1995).
- Z.H. Ming, Y.L. Soo, S. Huang, Y.H. Kao, J.C. Tsang, and S.S. Iyer, "Interfacial Microstructures of Ultrathin Ge Layers on Si Probed by X-ray Scattering and Fluorescence Yield", *Appl. Phys. Lett.*, 65, 1382, (1994).
- G. Oszlányi, G. Bortel, G. Faigel, M. Tegze, L. Gránásy, S. Pekker, P.W. Stephens, G. Bendele, R. Dinnebier, G. Mihály, A. Jánossy, O. Chauvet, and L. Forró, "Dimerization in K_1C_{60} and Rb_1C_{60} ", *Phys. Rev.*, B51, 12228, (1995).

Y.L. Soo, S.W. Huang, Z.H. Ming, Y.H. Kao, H. Munekata, and L.L. Chang, "Investigation of Local Structures Around Mn Atoms in $\text{In}_{1-x}\text{Mn}_x\text{As}$ Diluted Magnetic Semiconductors Using EXAFS", *Mat. Res. Soc. Symp. Proc.*, 375, 27, (1995).

Y.L. Soo, Z.H. Ming, S.W. Huang, Y.H. Kao, R.N. Bhargava, and D. Gallagher, "Local Structures Around Mn Luminescent Centers in Mn-doped Nanocrystals of ZnS", *Phys. Rev.*, B50, 7602, (1994).

M.A. Subramanian, M.K. Crawford, R.L. Harlow, T. Ami, J.A. Fernandez-Baca, Z.R. Wang, and D.C. Johnston, " Sr_2RhO_4 and Sr_2IrO_4 : Structural and Magnetic Studies of 4d and 5d Transition Metal Analogs of La_2CuO_4 ", *Physica C*, 235-240, 743, (1994).

T. Yildirim, J.E. Fischer, R. Dinnebier, P.W. Stephens, and C.L. Lin, "Fulleride Superconductors and Orientational Order: T_c vs. Lattice Constant in $\text{Na}_2\text{Rb}_x\text{Cs}_{1-x}\text{C}_{60}$ ", *Solid State Commun.*, 93, 269, (1995).

Beamline X3B2

T. Tse, P.W. Stephens, and P.J. Eng, "Epitaxy and Domain Growth of Pb on Ni(001)", *J. Phys. Condens. Mat.*, 6, 6111, (1994).

Beamline X4

T.E. Benson, D.J. Filman, C.T. Walsh, and J.M. Hogle, "An Enzyme-Substrate Complex Involved in Bacterial Cell Wall Biosynthesis", *Nature Struct. Biol.*, 2, 644-653, (1995).

F. Dyda, A.B. Hickman, T.M. Jenkins, A. Engelman, R. Craigie, and D.R. Davies, "Crystal Structure of the Catalytic Domain of HIV-1 Integrase: Similarity to Other Polynucleotidyl Transferases", *Science*, 266, 1981-1986, (1994).

M.M. Georgiadis, S.M. Jessen, C.M. Ogata, A. Telesnitsky, S.P. Goff, and W.A. Hendrickson, "Mechanistic Implications from the Structure of a Catalytic Fragment of Moloney Murine Leukemia Virus Reverse Transcriptase", *Structure*, 3, 879-892, (1995).

G. Ghosh, G. Van Duyne, S. Ghosh, and P.B. Sigler, "Structure of NF- κB p50 Homodimer Bound to a κB Site", *Nature*, 373, 303-310, (1995).

J. Goldberg, H.-B. Huang, Y.-G. Kwon, P. Greengard, A.C. Nairn, and J. Kuriyan, "Three-Dimensional Structure of the Catalytic Subunit of Protein Serine/Threonine Phosphatase-1", *Nature*, 376, 745-753, (1995).

S. R. Hubbard, L. Wei, L. Ellis, and W. A. Hendrickson, "Crystal Structure of the Tyrosine Kinase Domain of the Human Insulin Receptor", *Nature*, 372, 746-754, (1994).

T. S. R. Krishna, X.-P. Kong, S. Gary, P. M. Burgers, and J. Kuriyan, "Crystal Structure of the Eukaryotic DNA Polymerase Processivity Factor PCNA", *Cell*, 79, 1233-1243, (1994).

J. W. Lee, M. Chan, T. V. Law, H.J. Kwon, and B. K. Jap, "Preliminary Cryocrystallographic Study of the Mitochondrial Cytochrome bc_1 Complex: Improved Crystallization and Flash-cooling of a Large Membrane Protein", *J. Mol. Biol.*, 252, 15-19, (1995).

N. Q. McDonald, N. Panayotatos, and W.A. Hendrickson, "Crystal Structure of Dimeric Human Ciliary Neurotrophic Factor Determined by MAD Phasing", *EMBO J.*, 14, 2689-2699, (1995).

- C. W. Muller, F. A. Rey, M. Sodeoka, G. L. Verdine, and S.C. Harrison, "Structure of the NF- κ B p50 Homodimer bound to DNA", *Nature*, 373, 311-317, (1995).
- C. M. Ogata, and W.A. Hendrickson, "Protein Structures from MAD Experiments at the HHMI Beamline X4A at the NSLS", *Synch. Rad. News*, 8, 13-18, (1995).
- L. Shapiro, A. M. Fannon, P.D. Kwong, A. Thompson, M.S. Lehmann, G. Grubel, J.-F. Legrand, J. Als-Nielsen, D.R. Colman, and W. A. Hendrickson, "Structural Basis of Cell-cell Adhesion by Cadherins", *Nature*, 374, 327-337, (1995).
- J.-L. Staudenmann, W.L. Zotterman, D.W. Cook, C.M. Ogata, and W. A. Hendrickson, "The Howard Hughes Medical Institute Cassette for Storage Phosphor Plates", *Rev. Sci. Instrum.*, 65, 608-611, (1994).
- C. E. Stebbins, S. Borukhov, M. Oriova, A. Polyakov, A. Goldfarb, and S.A. Darst, "Crystal Structure of the GreA Transcript Cleavage Factor from *Escherichia coli*", *Nature*, 373, 636-640, (1995).
- T.M. Tanaka Hall, J. A. Porter, P. A. Beachy, and D.J. Leahy, "A Potential Catalytic Site Revealed by the 1.7-Å Crystal Structure of the Amino-Terminal Signalling Domain of Sonic Hedgehog", *Nature*, 378, 212-216, (1995).
- L. Tong, S. Pav, D. Lamarre, L. Pilote, S. LaPlante, P. C. Anderson, and F. Jung, "High Resolution Structures of Recombinant Human Renin in Complex with Polyhydroxymonoamide Inhibitors", *J. Mol. Biol.*, 250, 211-222, (1995).
- A. Qu, and D. J. Leahy, "Crystal Structure of the I-domain from the CD11a/CD18 (LFA-1, α , β 2) Integrin", *PNAS*, 92, 10277-10281, (1995).
- G. Zhang, M. G. Kazanietz, P. M. Blumberg, and J. H. Hurley, "Crystal Structure of the Cys2 Activator-Binding Domain of Protein Kinase C γ in Complex with Phorbol Ester", *Cell*, 81, 917-924, (1995).

Beamline X5

- G. Blanpied, M. Blecher, A. Caracappa, C. Djalali, G. Giordano, K. Hicks, S. Hoblit, M. Khandaker, O.C. Kistner, G. Matone, L. Miceli, C. Molinari, B. Preedom, D. Rebreyend, A.M. Sandorfi, C. Schaerf, R.M. Sealock, H. Ströher, C.E. Thorn, S.T. Thornton, C.S. Whisnant, H. Zhang, and X. Zhao, "Polarized Compton Scattering from the Proton", *Phys. Rev. Lett.*, 76, 1023-26, (1996).
- G. Blanpied, M. Blecher, A. Caracappa, C. Djalali, M.-A. Duval, G. Giordano, K. Hicks, S. Hoblit, M. Khandaker, A.M. Sandorfi, C. Schaerf, R.M. Sealock, C.E. Thorn, S.T. Thornton, K. Vaziri, C.S. Whisnant, and X. Zhao, "New Measurements of $2H(p,n)$ and Spin Problems in Coupled NA/NN Interactions", *Phys. Rev.*, C52, R455-59, (1995).
- A. Honig, Q. Fan, X. Wei, A.M. Sandorfi, and C.S. Whisnant, "New Investigations of Polarized Solid HD Targets", *Nucl. Inst. Meth. in Phys. Res.*, A356, 39-46, (1995).
- M. Khandaker, and A.M. Sandorfi, "Dependence of the Ratio of Electric to Magnetic $\Delta N\gamma$ Couplings on the Δ^+ Mass in Single-pion Photoproduction", *Phys. Rev.*, D51, 3966-68, (1995).

G.S. Adams, H. Baghaci, A. Caracappa, W. Clayton, A. D'Angelo, S. Hoblit, M. Khandaker, O.C. Kistner, T. Kobayashi, R. Lindgren, L. Miceli, C. Ruth, A.M. Sandorfi, C. Schaerf, R.M. Sealock, C. Smith, P. Stoler, D.J. Tedeschi, C.E. Thorn, S.T. Thornton, K. Vaziri, C.S. Whisnant, and E.J. Winhold, "Measurement of $\vec{\gamma}d \rightarrow p\pi\pi^0$ at Large Nucleon Momenta", *Phys. Rev.*, C51, 17-22, (1995).

A.M. Sandorfi, C.S. Whisnant, and M. Khandaker, "Incompatibility of Multipole Predictions for the Nucleon Spin-Polarizability and Drell-Hearn-Gerasimov Sum Rules", *Phys. Rev.*, D50, R6681, (1994).

Beamline X6A

G. Jennings, and P.L. Lee, "EX6AFS: A Data Acquisition System for High-Speed Dispersive EXAFS Measurements Implemented Using Object-Oriented Programming Techniques", *Rev. Sci. Instrum.*, 66, 1391-1393, (1995).

P.L. Lee, M.A. Beno, C.M. Ogata, G.S. Knapp, and G. Jennings, "Diffraction Applications Using the Energy Dispersive Beamline X6A at the National Synchrotron Light Source", *Rev. Sci. Instrum.*, 66, 1425-1427, (1995).

Beamline X6B

J. Bai, M. Tomkiewicz, and P.A. Montano, "Resonant X-reflectivity Measurements of a Ni/Fe Alloy Thin Film: a Composition Profile", *Zeitschrift fur Physik*, B97, 465, (1995).

M.A. Beno, G.S. Knapp, P. Armand, D.L. Price, and M.-L. Saboungi, "Application of New Synchrotron Powder Diffraction Techniques to Anomalous Scattering From Glasses", *Rev. Sci. Instrum.*, 66, 1308-1310, (1995).

J.M. Block, M.A. Baysal, A.B. Travis, and K. Slifer, "Transparent Nondiffracting Polarization Rotation Regime: A Synchrotron X-ray Study", *Phys. Rev. Lett.*, 75, 256-259, (1995).

W.B. Caldwell, D.J. Campbell, K. Chen, B.R. Herr, C.A. Mirkin, A. Malik, M.K. Durbin, P. Dutta, and K.G. Huang, "A Highly Order Self-Assembled Monolayer Film of an Azobenzenealkanethiol on Au(111): Electrochemical Properties and Structural Characterization by Synchrotron in-Plane X-ray Diffraction, Atomic Force Microscopy, and Surface-Enhanced Raman Spectroscopy", *J. Am. Chem. Soc.*, 117, 6071-6082, (1995).

L.X. Chen, Z. Wang, G. Hartwich, I. Katheder, H. Scheer, A. Scherz, P.A. Montano, and J.R. Norris, "An X-ray Absorption Study of Chemically Modified Bacterial Photosynthetic Reaction Centers", *Chem. Phys. Lett.*, 234, 437-444, (1995).

K.G. Huang, M. Ramanathan, and P.A. Montano, "Argonne National Laboratory X6B Beamline at NSLS: A Versatile Facility", *Rev. Sci. Instrum.*, 66, 1688-1690, (1995).

K.G. Huang, J. Zegenhagen, J.M. Phillips, and J.R. Patel, "Two Dimensional Structural Modulation of Epitaxial CaF₂ Overlayers on Si(111)", *Phys. Rev. Lett.*, 72, 2430, (1994).

Q.D. Jiang, K.G. Huang, M. Rao, and J. Zegenhagen, "The Initial Stage of the Epitaxial Growth of RBa₂Cu₃O_{7-x} Thin Films", *Physica C*, 235-240, 677-678, (1994).

M. Ramanathan, and P.A. Montano, "Versatile Double-Crystal Fixed Exit Monochromator for X-ray Synchrotron Radiation", *Rev. Sci. Instrum.*, 66, 1754-1756, (1995).

I. Song, B. Rickett, P. Janavicius, J.H. Payer, and M.R. Antonio, "In situ Total-Electron-Yield Sulfur K-edge XAFS Measurements During Exposure of Copper to an SO₂-containing Humid Atmosphere", *Nucl. Instrum. Meth. Phys. Res.*, A360, 634-641, (1995).

I. Song, M.R. Antonio, and J.H. Payer "An Iron K-edge XANES Study of Iron and Iron Oxides for the Cathodic Disbonding of Fusion Bonded Epoxy in Alkaline Aqueous Solution", *J. Electrochem. Soc.*, 142, 2219-2224, (1995)

Beamline X7A

T. Ami, M.K. Crawford, R.L. Harlow, Z.G. Li, T. Vogt, Q. Zhu, and D.E. Cox, "A Neutron and Synchrotron X-ray Scattering Study of Sr₂CuO_{3.8} Synthesized under Moderate Pressure: a New Compound Related to Superconducting Sr₂CuO_{3.1}", *Physica*, C235/240, 1003, (1994).

T. Ami, M.K. Crawford, R.L. Harlow, Z. Wang, D.C. Johnston, Q. Huang, and R.C. Erwin, "Magnetic Susceptibility and Low Temperature Structure of the Linear Chain Cuprate Sr₂CuO₃", *Phys. Rev.*, B51, 5994, (1995).

C. Bezou, A. Nonat, J.-C. Mutin, A.N. Christensen, and M.S. Lehmann, "Investigation of the Crystal Structure of $\sqrt{2}$ -CaSO₄, CaSO₄-0.5H₂O, and CaSO₄-0.6H₂O by Powder Diffraction Methods", *J. Solid State Chem.*, 117, 165, (1995).

K. Breuer, D.M. Goldberg, K.E. Smith, M. Greenblatt, and W. McCarroll, "Resonant Photoemission Study of the Electronic Structure of K_{0.3}MoO₃", *Solid State Comm.*, 94, 601, (1995).

R.W. Broach, N.K. McGuire, C.C. Chao, and R.M. Kirchner, "Direct Methods Structure Determination From Synchrotron Powder Diffraction Data of a New Clathrasil, TMA Silicate", *J. Phys. Chem. Solids*, 57/10, 1363, (1995).

M.K. Crawford, R.L. Harlow, E.M. McCarron, D.E. Cox, and Q. Huang, "Effects of Structural Phase Transitions on Superconductivity and Magnetism in Substituted Derivatives of La₂CuO₄", *Physica*, C235-240, 170, (1994).

M.K. Crawford, R.L. Harlow, E.M. McCarron, N. Herron, W.E. Farneth, W. Donahue, B.A. Parkinson, and J. Schirber, "Synchrotron X-ray Powder Diffraction Study of Electrochemically Oxidized La₂CuO_{4.8} and La_{2-x}Nd_xCuO_{4.8}", *J. Phys. Chem. Of Solids*, 56, 1459, (1995).

T. Egami, "Determining Medium Range Order by Powder Diffraction", *J. Phys. Chem. Solids*, 56, 1407, (1995).

L.W. Finger, D.E. Cox, and A.P. Jephcoat, "A Correction for Powder Diffraction Peak Asymmetry Due to Axial Divergence", *J. Appl. Cryst.*, 27, 892, (1994).

L.W. Finger, R.M. Hazen, and B.A. Fursenko, "Refinement of Crystal Structure of BaSi₄O₉ in the Benitoite Form", *J. Phys. Chem. Solids*, 56/10, 1389, (1995).

J. E. Fischer, "Intercalation Compounds of Solid C₆₀", *Phys. & Chem. Of Fullerenes*, edited by K. Prassides, NATO ASI Series, 443, 223, (1995).

J.E. Fischer, G. Bendele, R. Dinnebier, P.W. Stephens, C.L. Lin, N. Bykovetz, and Q. Zhu, "Structural Analysis of Fullerene and Fulleride Solids from Synchrotron X-ray Powder Diffraction", *J. Phys. Chem. Solids*, 56, 1445, (1995).

- N. Herron, D.L. Thorn, and R.L. Harlow, "Molecular Precursors to Functional Materials", Molecularly Designed Ultrafine/Nanostructured Materials, edited by K.E. Gonsalves, MRS Symp. Proc., 351, 31, (1994).
- N. Herron, D.L. Thorn, R.L. Harlow, G.A. Jones, J.B. Parise, J.A. Fernandez-Baca, and T. Vogt, "Preparation and Structural Characterization of Two New Phases of Aluminum Trifluoride", *Chem. Mater.*, 7, 75, (1995).
- R.M. Kirchner, and J.M. Bennett, "The Structure of Calcined AlPO_4 -41: a New Framework Topology Containing One-Dimensional 10-Ring Pores", *Zeolites*, 14, 523, (1994).
- S.J. LaPlaca, J.F. Bringley, B.A. Scott, and D.E. Cox, "Structure of $\text{La}_3\text{Cu}_5\text{O}_{13.35}$ by High Resolution Synchrotron X-ray Diffraction", *J. Solid State Chem.*, 118, 170, (1995).
- K. Leinenweber, J. Linton, A. Navrotsky, Y. Fei, and J.B. Parise, "High-Pressure Perovskites on the Join CaTiO_3 - FeTiO_3 ", *Phys. and Chem. Minerals*, 22, 251, (1995).
- K. Leinenweber, and J.B. Parise, "High-Pressure Synthesis and Crystal Structure of $\text{CaFeTi}_2\text{O}_6$, a new Perovskite Structure Type", *J. Solid State Chem.*, 114, 277, (1995).
- R.F. Lobo, M. Pan, I. Chan, R.C. Medrud, S.I. Zones, P.A. Crozier, and M.E. Davis, "Physicochemical Characterization of Zeolites SSZ-26 and SSZ-33", *J. Phys. Chem.*, 98, 12040, (1994).
- N.K. McGuire, C.A. Bateman, C.S. Blackwell, and S.T. Wilson, "Structure Refinement, Electron Microscopy, and Solid-State Magic Angle Spinning Nuclear Magnetic Resonance Characterization of AlPO_4 -52: An Aluminophosphate with a Large Cage", *Zeolites*, 15, 460, (1995).
- R.E. Morris, J.J. Owen, and A.K. Cheetham, "The Structure of $\text{La}_4\text{Ti}_9\text{O}_{24}$ from Synchrotron X-ray Powder Diffraction", *J. Phys. Chem. Solids*, 56/10, 1297, (1995).
- R.E. Morris, S.J. Weigel, N.J. Henson, L.M. Bull, and A.K. Cheetham, "A Synchrotron X-ray Diffraction, Neutron Diffraction, ^{29}Si MAS NMR, and Computational Study of the Siliceous Form of Zeolite Ferrierite", *J. Am. Chem. Soc.*, 116, 11849, (1994).
- J.B. Parise, D.R. Corbin, and L. Abrams, "Structural Changes Upon Sorption and Desorption of Xe from Cd-Exchanged Zeolite rho: A Real-time Synchrotron X-ray Powder Diffraction Study", *Microporous Materials*, 4, 99, (1995).
- J.-H. Park, and J.B. Parise, "High-Pressure Synthesis and Structure of a new Aurate, CaAu_2O_4 ", *Chem. Mater.*, 7, 1055, (1995).
- D.M. Poojary, D. Grohol, and A. Clearfield, "Crystal Structure of Uranyl Chloromethylphosphonate from X-ray Powder Diffraction Data", *J. Phys. Chem. Solids*, 56/10, 1383, (1995).
- D.M. Poojary, B. Zhang, and A. Clearfield, "Structure of a Mixed Phosphate/Phosphonate Layered Compound from Synchrotron X-ray Powder Diffraction Data", *Angew. Chem.*, 33, 2324, (1994).
- H.D. Rosenfeld, and T. Egami, "A Model of Short and Intermediate Range Atomic Structure in the Relaxor Ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ", *Ferroelectrics*, 158, 351, (1994).
- H.D. Rosenfeld, and T. Egami, "Short and Intermediate Range Structural and Chemical Order in the Relaxor Ferroelectric Lead Magnesium Niobate", *Ferroelectrics*, 164, 133, (1995).

D. Sandford, M. Fendorf, A.M. Stacy, W.L. Holstein, and M.K. Crawford, "Observation of Hendricks-Teller Partial Order in a Tetragonal Cuprate Superconductor: $\text{La}_{1.68}\text{Nd}_{0.14}\text{Na}_{0.10}\text{K}_{0.082}\text{CuO}_4$ ", *Phys. Rev.*, B50, 9419, (1994).

J.E. Schirber, W.R. Bayless, A.R. Kortan, E. Ozdas, O. Zhou, D. Murphy, and J.E. Fischer, "Pressure Studies of Alkali, Alkaline Earth and Rare Earth Doped C_{60} Superconductors", *Science and Technology of Fullerene Materials*, edited by P. Bernier, T.W. Ebbesen, D.S. Bethune, R.M. Metzger, L.Y. Chiang, and J.W. Mintmire, *MRS Symp. Proc.*, 359, p. 289, (1995).

G.C. Smith, D.E. Cox, and A.P. Jephcoat, "X-ray Position Resolution in Proportional Chambers in the Region of 100 μm (FWHM) Above the Xenon K-edge", *Nucl. Instrum. And Meth.*, A350, 621, (1994).

M.A. Subramanian, M.K. Crawford, R.L. Harlow, T. Ami, J.A. Fernandez-Baca, Z.R. Wang, and D.C. Johnston, " Sr_2RhO_4 and Sr_2IrO_4 : Structural and Magnetic Studies of 4d and 5d Transition Metal Analogs of La_2CuO_4 ", *Physica*, C235/240, 743, (1994).

T. Yildirim, L. Barbedette, J.E. Fischer, C.L. Lin, P.W. Stephens, and P.E. Sulewski, "Structure-Property Correlations in Fullerene Intercalation Compounds", *Physics and Chemistry of Fullerenes and Derivatives*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth, World Scientific, Singapore, p. 379, (1995).

T. Yildirim, L. Barbedette, K. Kniaz, J.E. Fischer, C.L. Lin, N. Bykovetz, P.W. Stephens, P.E. Sulewski, and S.C. Erwin, "Fullerene Superconductors: Effects of Molecular Orientation and Valence", *Science and Technology of Fullerene Materials*, edited by P. Bernier, T.W. Ebbesen, D.S. Bethune, R.M. Metzger, L.Y. Chiang, and J.W. Mintmire, *MRS Symp. Proc.*, 359, p. 273, (1995).

Q. Zhu, "Pressure-induced Polymerization of Ternary Fulleride Superconductors", *Phys. Rev.*, B52, R723, (1995).

Q. Zhu, D.E. Cox, and J.E. Fischer, "Phase Transitions in KC_{60} : Dimer Formation via Rapid Quenching", *Phys. Rev.*, B51, 3966, (1995).

Beamline X7B

J. Aizenberg, L. Addadi, J. Hanson, L. Leiserowitz, T.F. Koetzle, and S. Weiner, "Morphogenesis of Calcitic Sponge Spicules: A Role for Specialized Proteins Interacting with Growing Crystals", *FASEB J.*, 9, 262-268, (1995).

S. Åsbrink, J.C. Hanson, A. Waskowska, and I. Uszynski, "Remarks on the Diffraction by the Diamonds of the High-Pressure Diamond-Anvil Cell", *High Pressure Res.*, 12, 171-174, (1994).

A.N. Christensen, P. Norby, and J.C. Hanson, "Chemical Reactions in the System $\text{MgO-MgCl}_2\text{-H}_2\text{O}$ Followed by Time Resolved Synchrotron X-Ray Powder Diffraction", *J. Solid State Chem.*, 114, 556, (1995).

J. Kansikas, I. Mutikaninen, U. Long, M. Nelson and Å. Kvik, "Synchrotron X-ray Structure of a Zeolite ZSM-39 Analogue", *Bull. Soc. Cat. Cien*, 13, 121-126, (1994).

J.Z. Larese, and Q.M. Zhang, "Phase Transitions of Argon Multilayer Films on Graphite: Evolution from Multilayer Film to Bulk Solid", *Phys. Rev.*, B51, 17023-17027, (1995).

V.N. Molchanov, R.A. Tamazyen, V.I. Simonov, M.K. Blomberg, M.J. Merisalo, and V.S. Mironov, "Structure and Superconductivity in $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ ", *Physica C*, 229, 331-345, (1994).

Beamline X8A

D.V. Morgan, R.J. Bartlett, and M. Sagurton, "Single-Photon Multiple Ionization of Argon in the K-edge Region", *Phys. Rev.*, A51, 2939, (1995).

M. Sagurton, R.J. Bartlett, J.A.R. Samson, Z.X. He, and D. Morgan, "Effect of Compton Scattering on the Double-to-Single Photoionization Ratio in Helium", *Phys. Rev.*, A52, 2829, (1995).

Beamline X8C

R.W. Alkire, E.P. Sullivan, F.D. Michaud, W.J. Trela, R.J. Bartlett, and R. Rothe, "Performance of Beamline X8C at the NSLS", *Nucl. Instr. And Meth. In Phys. Res.*, A352, 535-541, (1994).

O. El-Kabbani, K. Judge, S.L. Ginell, L.J. DeLucas, and T.G. Flynn, "Crystallization and Preliminary Structure of Porcine Aldehyde Reductase/NADPH Binary Complex", *Acta Cryst.*, D51, 605-608, (1995).

O. El-Kabbani, K. Judge, S.L. Ginell, D.A.A. Myles, L.J. DeLucas, and T.G. Flynn, "Structure of Porcine Aldehyde Reductase Holoenzyme", *Nature Struct. Bio.*, 2, 687-692, (1995).

L. Tabernero, C.Y. Chang, S.L. Ohringer, W.F. Lau, E.J. Iwanowicz, W. Han, T.C. Wang, S.M. Seiler, D.G.M. Roberts, and J.S. Sack, "Structure of a Retro-binding Peptide Inhibitor Complexed with Human Alpha-Thrombin", *J. Mol. Biol.*, 246, 14-20, (1995).

Beamline X9B

J.C. Andrews, R. Cinco, H. Dau, M.J. Latimer, W. Liang, T. A. Roelofs, A. Rompel, V.K. Yachandra, K. Sauer, and M.P. Klein, "Photosynthetic Water Oxidation: Structural Insights to the Catalytic Manganese Complex", *Physica B*, 208, 657-659, (1995).

D.S. Auld, and K. Zhang, "Making Zinc Visible", *FASEB J.*, Vol. 9, A1326, (1995).

M.J. Baldwin, T.L. Stemmler, P.J. Riggs-Gelasco, M.L. Kirk, J.E. Penner-Hahn, and V.L. Pecoraro, "Structural and Magnetic Effects of Successive Protonations of Oxo Bridges in High Valent Manganese Dimers", *J. Am. Chem. Soc.*, 116, 11349-11356, (1994).

T.M. Barnhart, and J.E. Penner-Hahn, "EXAFS Characterization of Methyl and Phenyl Cuprates in Solution", *Physica B*, 208-209, 709-710 (1995).

J. Briggs, and M. Caffrey, "The Temperature-Composition Phase Diagram and Mesophase Structure Characterization of Monopentadecenoin in Water", *Biophys. J.*, 67, 1594-1602, (1994).

J. A. Chupa, J.P. McCauley, Jr., R.M. Strongin, A.B. Smith, III, J.K. Blasie, L.J. Peticolas, and J.C. Bean, "Vectorially Oriented Membrane Protein Monolayers: Profile Structures via X-ray Interferometry/Holography", *Biophys. J.*, 67, 336-348, (1994).

J.A. Chupa, J.P. McCauley, R.M. Strongin, A.B. Smith, J.K. Blasie, L.J. Peticolas, and J.C. Bean, "Vectorially Oriented Membrane Protein Monolayers: Profile Structure via X-Ray Interferometry/Holography", *Biophys. J.*, 67, 336-348, (1994).

- K. Clark, J.E. Penner-Hahn, M. Whittaker, and J.W. Whittaker, "Structural Characterization of the Copper Site in Galactose Oxidase Using X-ray Absorption Spectroscopy", *Biochemistry*, **33**, 12553-12557, (1994).
- G. Czerlinski, M. Isaacson, R. Ramires, S. Chen, B. Kanagal, C. Venkatesh, and L. Powers, "A Fast Micro-Flow Apparatus", *Rev. Sci. Instrum.*, **66**, 2604, (1995).
- H. Dau, J.C. Andrews, T. A. Roelofs, M.J. Latimer, W. Liang, V.K. Yachandra, K. Sauer, and M.P. Klein, "Structural Consequences of Ammonia Binding to the Manganese Center of the Photosynthetic Oxygen Evolving Complex: An X-Ray Absorption Study of Isotropic and Oriented Photosystem II Particles", *Biochemistry*, **34**, 5274-5287, (1995).
- V.J. DeRose, M.J. Latimer, J.L. Zimmermann, I. Mukerji, V.K. Yachandra, K. Sauer, and M.P. Klein, "Fluoride Substitution in the Mn Cluster from Photosystem II: EPR and X-Ray Absorption Spectroscopy Studies", *Chem. Phys.*, **194**, 443-459, (1995).
- J. Dong, and K. Zhang, "A Method for Constructing Unknown Orientation Dependent Spectra from a Group of Spectra in Polarized XAFS Experiments", *Physica B*, **208/209**, 161-165, (1995).
- Y. Dong, H. Fujii, M.P. Hendrich, R.A. Leising, G. Pan, C.R. Randall, E.C. Wilkinson, Y. Zang, L. Que, Jr., B.G. Fox, K. Kauffmann, and E. Munck, "A High-Valent Nonheme Iron Intermediate. Structure and Properties of $[\text{Fe}_2(\mu\text{-O})_2(5\text{-Me-TPA})_2](\text{ClO}_4)_3$ ", *J. Am. Chem. Soc.*, **117**, 2778-2792, (1995).
- B.A. Eipper, A.S. Quon, R.E. Mains, J.S. Boswell, and N.J. Blackburn, "The Catalytic Core of Peptidylglycine Alpha-Hydroxylating Monooxygenase: Investigation by Site-Directed Mutagenesis, Cu X-Ray Absorption Spectroscopy, and Electron Paramagnetic Resonance", *Biochemistry*, **34**, 2857-2865, (1995).
- Z. Farhangrazi, B. Copeland, T. Nakayama, T. Amachi, I. Yamazaki, and L. Powers, "Oxidation-Reduction Properties of Compounds I and II of *Arthrobacter Ramosus* Peroxidase", *Biochem.*, **33**, 5647, (1994).
- Z. Farhangrazi, M. Fossett, L. Powers, and W. Ellis, "Variable-Temperature Spectroelectrochemical Study of Horseradish Peroxidase", *Biochem.*, **34**, 2866, (1995).
- N. Kitajima, N. Tamura, H. Amagai, H. Fukui, Y. Moro-oka, Y. Mizutani, T. Kitagawa, R. Methur, K. Heerwegh, C.A. Reed, C.R. Randall, L. Que, Jr., and K. Tatsumi, "Monomeric Carboxylate Ferrous Complexes as Models for the Dioxygen Binding Sites in Non-Heme Iron Proteins. The Reversible Formation and Characterization of μ -Peroxo Diferric Complexes", *J. Am. Chem. Soc.*, **116**, 9071-9085, (1994).
- M.P. Klein, "Perspectives on Magnetic Resonance and X-ray Absorption Spectroscopy", in Biochemistry. Biochemical Spectroscopy, Methods in Enzymology, edited by K. Sauer, Academic Press, **246**, 529-536, (1994).
- R. Koynova, and M. Caffrey, "Phases and Phase Transitions of the Hydrated Phosphatidylethanolamines", *Chem. Phys. Lipids*, **69**, 1-34, (1994).
- R. Koynova, and M. Caffrey, "Phases and Phase Transitions of the Hydrated Glycoglycerolipids", *Chem. Phys. Lipid*, **69**, 181-207, (1994).
- R. Koynova, and M. Caffrey, "Phases and Phase Transitions of the Hydrated Sphingolipids", *Biochim. Biophys. Acta*, **1255**, 213-236, (1995).
- J. Landro, E. Schmidt, P. Schimmel, D.L. Tierney, and J.E. Penner-Hahn, "Thiol Ligation of Two Zinc Atoms to a Class II tRNA Synthetase: Evidence for Unshared Thiols and Role in Amino Acid Binding and Utilization", *Biochemistry*, **33**, 14213-14220, (1994).

- M.J. Latimer, A. Rompel, J.H. Underwood, V.K. Yachandra, and M.P. Klein, "A Simple In-Hutch Assembly for X-ray Harmonic Suppression", *Rev. Sci. Instrum.*, 66, 1843-1845, (1995).
- M.J. Latimer, V.J. DeRose, I. Mukerji, V.K. Yachandra, K. Sauer, and M.P. Klein, "Evidence for the Proximity of Calcium to the Manganese Cluster of Photosystem II: Determination by X-Ray Absorption Spectroscopy", *Biochemistry*, 34, 10898-10909, (1995).
- M.J. Latimer, The Role of Calcium in the Oxygen Evolving Center of Photosystem II, PhD. Dissertation, University of California, Berkeley, CA (1995).
- W. Liang, Structural and Oxidation State Studies of the Manganese Cluster in the Oxygen Evolving Complex of Photosystem II, PhD. Dissertation, University of California, (1995). LBL-Report 36632
- M. Lorenz, K.J. Poole, D. Popp, G. Rosenbaum, and K.C. Holmes, "An Atomic Model of the Unregulated Thin Filament Obtained by X-Ray Fiber Diffraction on Oriented Actin-Tropomyosin Gels", *J. Mol. Biol.*, 246, 108-119, (1995).
- H.D. Lujan, M.R. Mowatt, J.J. Wu, Y. Lu, A. Lees, M.R. Chance, and T.E. Nash, "Purification of a Variant-Specific Surface Protein of *Giardia Lamblia* and Characterization of its Metal-Binding Properties", *J. Biol. Chem.*, 270, 13807-13813, (1995).
- S. Mahapatra, J.A. Halfen, E.C. Wilkinson, G. Pan, C.J. Cramer, L. Que, and W.B. Tolman, "A New Intermediate in Copper Dioxygen Chemistry: Breaking the O-O Bond to Form a $(\text{Cu}_2(\mu\text{-O}_2))^{2+}$ Core", *J. Am. Chem. Soc.*, 117, 8865-8866, (1995).
- N.C. Maliszewskyj, P.A. Heiney, J.Y. Josefowicz, T. Plesnivý, H. Ringsdorf, and P. Schuhmacher, "Structure of Langmuir Blodgett Films of Star-Shaped Oligomeric Discogens", *Langmuir*, 11, 1666-1674, (1995).
- L.M. Miller, and M.R. Chance, "Structural and Electronic Factors That Influence Oxygen Affinities: A Spectroscopic Comparison of Ferrous & Cobaltous Myoglobin", *Biochemistry*, 34, 10170-10179, (1995).
- L.M. Miller, Distal and Proximal Control of Oxygen Binding and Release in Hemeproteins, PhD. Dissertation, Albert Einstein College of Medicine, June 1995.
- I. Mukerji, J.C. Andrews, V.J. DeRose, M.J. Latimer, V.K. Yachandra, K. Sauer, and M.P. Klein, "Orientation of the Oxygen-Evolving Manganese Complex in a Photosystem II Membrane Preparation: An X-ray Absorption Spectroscopy Study", *Biochemistry*, 33, 9712-9721, (1994).
- K.J. Poole, K.C. Holmes, G. Evans, G. Rosenbaum, I. Rayment, and M. Lorenz, "Control of the Actomyosin Interaction", *Biophysical J.*, 68, 348S, (1995).
- L. Powers, M. Lauraeus, K.S. Reddy, B. Chance, and M. Wikstrom, "Structure of the Binuclear Heme Iron-Copper Site in the Quinol-oxidizing Cytochrome aa₃, from *Bacillus subtilis*", *Biochim. Biophys. Acta*, 1183, 504-512, (1994).
- C.R. Randall, L. Shu, Y.M. Chiou, K.S. Hagen, M. Ito, N. Kitajima, R.J. Lachicotte, Y. Zang, and L. Que, Jr. "X-Ray Absorption Pre-Edge Studies of High-Spin Iron (II) Complexes", *Inorg. Chem.*, 34, 1036-1039, (1995).
- R.S. Rowlett, M.R. Chance, M.D. Wirt, J.R. Royal, M. Woodroffe, Y.A. Wang, R.P. Saha, and M.G. Lam, "Kinetic and Structural Characterization of Spinach Carbonic Anhydrase", *Biochemistry*, 33, 13967-13976, (1994).

R.C. Scarrow, M.G. Trimitsis, C.P. Buck, G.N. Grove, R.A. Cowling, and M.J. Nelson, "X-Ray Spectroscopy of the Iron Site in Soybean Lipoxygenase-1: Changes in Coordination upon Oxidation or Addition of Methanol", *Biochemistry*, 33, 15023-15035, (1994).

E.M. Scheuring, Structural and Electronic Effects in Cobalamins and Model Compounds: Their Importance in the Enzymatic Processes, PhD. Dissertation, Albert Einstein College of Medicine, May 1995.

L. Shu, Y.M. Chiou, A.M. Orville, M.A. Miller, J.D. Lipscomb, and L. Que, Jr. "X-Ray Absorption Spectroscopic Studies of the Fe(II) Active Site of Catechol 2,3-Dioxygenase. Implications for the Extradiol Cleavage Mechanism", *Biochemistry*, 34, 6649-6659, (1995).

H.L. Tang, B. Chance, A. Mauk, L. Powers, K.S. Reddy, and M. Smith, "Spectroscopic, Electrochemical, and Ligand Binding Properties of the Horse Heart Metmyoglobin His64Try Variant", *Biochim. Biophys. Acta*, 1206, 90-96, (1994).

D.L. Tierney, J.A. Fee, M.L. Ludwig, and J.E. Penner-Hahn, "X-Ray Absorption Spectroscopy of the Iron Site in Escherichia Coli Fe(III) Superoxide Dismutase", *Biochemistry*, 34, 1661-1668, (1995).

J. Wang, and M. Caffrey, "Locating Calcium in Membranes with X-Ray Standing Waves", *J. Am. Chem. Soc.*, 117, 3304-3305, (1995).

X. Wang, Spectroscopic Studies of Uteroferrin and Its Substrate Analogues, MS Thesis, University of Minnesota, 1995.

M.D. Wirt, M. Kumar, J.J. Wu, E.M. Scheuring, S.W. Ragsdale, M.R. Chance, "Structural and Electronic Factors in Heterolytic Cleavage: Formulation of the Co(I) Intermediate in the Corrinoid Protein from Clostridium Thermoaceticum", *Biochemistry*, 34, 5269-5273, (1995).

V.K. Yachandra, K. Sauer, and M.P. Klein, "Recent Studies on the Mn Complex Involved in Photosynthetic Water Oxidation", Proc. of the US-Japan Binational Conference on Dynamic Aspects of the Photochemical Reaction Center, Toyko, Japan. p. 32, (1995).

V.K. Yachandra, "X-ray Absorption Spectroscopy and Applications in Structural Biology" in Biochemical Spectroscopy, Methods in Enzymology, edited by K. Sauer, Academic Press, 246, 638-675, (1994).

K. Zhang, J. Dong, and D.S. Auld, "A Time-Resolved Study of Substrate Hydrolysis by Carboxypeptidase A", *Physica B*, 208/209, 719-721, (1995).

X.Y. Zhang, M.T. Pope, M.R. Chance, and G.B. Jameson, "High-Valent Manganese in Polyoxotungstates. 1. Manganese (IV) Keggin Derivatives", *Polyhedron*, 14, 1381-1392, (1995).

Beamline X10A

P. Fenter, P.E. Burrows, P. Eisenberger, and S. Forrest, "Layer by Layer, Quasi-Epitaxial Growth of a Crystalline Organic Thin Film", *J. Cryst. Growth*, 152, 65, (1995).

P. Fenter, A. Eberhardt, and P. Eisenberger, "n-Alkyl Thiols Self-Assemble as Disulfides on Au(111)", *Science*, 266, 1216, (1994)

M. Linford, R.M. Weymouth, P. Fenter, P. Eisenberger, and C.E.D. Chidsey, "Alkyl Monolayers on Silicon: Reaction of 1-Alkenes with Hydrogen Terminated Silicon", *J. Amer. Chem. Soc.*, 117, 3145, (1995).

G.-Y. Liu, P. Fenter, C.E.D. Chidsey, D.F. Ogletree, P. Eisenberger, and M. Salmeron, "An Unexpected Packing of Fluorinated n-Alkane Thiols on Au(111): A Combined Atomic Force Microscopy and X-ray Diffraction Study", *J. Chem. Phys.*, 101, 4301, (1994).

C.A. Melendres, Y.P. Feng, D.D. Lee, and S.K. Sinha, "X-ray Diffuse Scattering for the *in situ* Study of Electrochemically Induced Pitting on Metal Surfaces", *J. Electrochem. Soc.*, 142, L19, (1995).

Beamline X10C

G. Meitzner, and J. Sinfelt, "X-Ray Absorption Studies of the Electronic Structures of Pd-Ag and Pd-Au Alloys", *Catal. Letts.*, 30, 1, (1995).

Beamlines X11A & X11B

M. Balasubramanian, Y.D. Zhang, J.I. Budnick, K.E. Gonsalves, and T.D. Xiao, "Studies on Nanostructured M50 Type Steel Using X-ray Absorption Spectroscopy and NMR", *Mat. Res. Soc. Symp. Proc.*, 195, 351, (1994).

M. Balasubramanian, D.M. Pease, J.I. Budnick, T. Manzur, and D.L. Brew, "Local Environment of Transition Metal Ternary Dopants in β Phase Transition Metal Aluminides", *Physica*, B208/209, 493, (1995).

M. Balasubramanian, Y.D. Zhang, J.I. Budnick, and D.M. Pease, "Local Environment of Fe in Nanostructured M50 Type Steel Samples", *Nanostructured Mat.*, 249, 5, (1995).

M. Balasubramanian, D.M. Pease, J.I. Budnick, T. Manzur, and D.L. Brew, "Site Occupation Tendencies for Ternary Additions (Fe, Co, Ni) In β Phase Transition Metal Aluminides", *Phys. Rev.*, B51, 8102, (1995).

D.L. Brew, D.M. Pease, and J.I. Budnick, "Corrections of Residual Fluorescence Distortions for a Glancing-Angle X-ray Absorption Technique", *Phys. Rev.*, B50, 9025, (1994).

M. Endregard, D.G. Nicholson, M. Stocker, and G. Lamble, "Absorption and Thermal Decomposition of Cobaltcenium Ions on Microporous AlPO_4 Studied by XAS 13C Solid State NMR and FT-IR", *J. Mater. Chem.*, 5, 785, (1995).

M. Endregard, D.G., Nicholson, M. Stocker, and G. Lamble, "Cobaltcenium Ions Absorbed on Large-Pore Aluminophosphate VPI-5 Studied by XAS, 13C Solid-State NMR and FT-IR", *J. Mater. Chem.*, 5, 485, (1995).

A. Frenkel, V. Voronel, A. Katzir, M. Newville, and E.A. Stern, "Buckled Crystalline Structure of Disordered Mixed Salts", *Physica*, B208/209, 334, (1995).

A. Frenkel, A. Rubshrein, V. Voronel, and E.A. Stern, "Comparative Radial-Distribution Analysis of the Short Range Order in Metallic Glass $\text{Al}_{0.91}\text{La}_{0.09}$ and Crystalline $\text{Al}_{11}\text{La}_3$ ", *Physica*, B208/209, 398, (1995).

S.M. Heald, J.E. Amonette, G.D. Truner, and A.D. Scott, "An XAFS Study of the Oxidation of Structural Iron in Biotite Mica by Solutions Containing Br_2 or H_2O_2 ", *Physica*, B208/209, 604, (1995).

D.T. Jiang, Z.Q. Gui, S.M. Heald, T.K. Sham, and M.J. Stillman, "XAFS of Silver(I) Metallothionein", *Physica*, B208/209, 729, (1995).

D.T. Jiang, S.M. Heald, T.K. Sham, and M.J. Stillman, "Structures of the Cadmium, Mercury, and Zinc Thiolate Clusters in Metallothionein: XAFS Study of $\text{Zn}_7\text{-Mt}$, $\text{Cd}_7\text{-Mt}$, $\text{Hg}_7\text{-MT}$, and $\text{Hg}_{18}\text{-MT}$ Formed From Rabbit Liver Metallothionein", *J. Am. Chem. Soc.*, 116, 11004, (1994).

- D.T. Jiang, T.K. Sham, P.R. Norton, and S.M. Heald, "Charge Redistribution in AuZn: An X-ray-Absorption Near-Edge-Structure Study", *Phys. Rev.*, B49, 3709, (1994).
- S. Kawi, O. Alexeev, M. Shelef, and B.C. Gates, "Highly Dispersed MgO-Supported Model Pd-Mo Catalysts Prepared From Bimetallic Clusters", *J. of Phys. Chem.*, 99, 6926, (1995).
- S. Kawi, J.-R. Chang, and B.C. Gates, "Cluster Catalysis: Propane Hydrogenolysis Catalyzed by MgO-Supported Tetrairidium", *J. of Phys. Chem.*, 98, 12978, (1994).
- S. Kawi, and B.C. Gates, "Tetra- and Hexairidium Clusters in NaX Zeolite Cages: Synthesis, Reactivity, and Characterization by Infrared and Extended X-ray Absorption Fine Structure Spectroscopies", *J. of Phys. Chem.*, 99, 8824, (1995).
- K.M. Kemner, and B.A. Bunker, "Gas-Amplified Electron-Yield X-ray Detection at Low Temperatures", *Rev. Sci. Instrum.*, 65, 3667, (1994).
- K.M. Kemner, B.A. Bunker, H. Luo, N. Samarth, J.K. Furdyna, M.R. Weidmann, and K.E. Newman, "Atomic Rearrangement at Interfaces in ZnTe/CdSe Superlattices", *Phys. Rev.*, B50, 4327, (1994).
- G.M. Lamble, "Design and Operation of a UHV Double-Bounce Harmonic Rejection Mirror for XAFS Studies", *Rev. Sci. Instrum.*, 66, 1422, (1995).
- G.M. Lamble, "Workshop on Techniques and Experimental Methods for X-ray Absorption Fine Structure Spectroscopy", *Rev. Sci. Instrum.*, 66, 2383, (1995).
- G.M. Lamble, J.F. Lee, W.J. Staudt, and R.J. Reeder, "Structural Studies of Selenate Incorporation into Calcite Crystals", *Physica*, B208/209, 589, (1995).
- J.F. Lee, S. Bajt, S.B. Clark, G.M. Lamble, C.A. Langton, and L. Oji, "Chromium Speciation in Hazardous Cement-based Waste Forms", *Physica*, B208/209, 577, (1995).
- A. Lund, D.G. Nicholson, G. Lamble, and B. Beagley, "X-Ray Absorption Spectroscopic Study of the AlPO_4^{-5} : Ferrocene Inclusion Compound and its Thermally Decomposed Products", *J. Mater. Chem.*, 4, 1723, (1994).
- A. Lund, D.G. Nicholson, R.V. Parish, and J. Wright, " ^{57}Fe Mossbauer Spectroscopic Studies of the Ferrocene Molecular Reorientation in AlPO_4^{-5} and AlPO_4^{-8} Frameworks", *Acta Chem. Scand.*, 48, 738, (1994).
- A.N. Mansour, and C.A. Melendres, "XAFS Investigation of the Structure and Valency of Nickel in some Oxycompounds", *Physica*, B208/209, 583, (1995).
- A.N. Mansour, C.-P. Wong, and R.A. Brizzolara, "Atomic Structure of Amorphous $\text{Al}_{100-2x}\text{Co}_x\text{Ce}_x$ ($x=8,9$, and 10) and $\text{Al}_{80}\text{Fe}_{10}\text{Ce}_{10}$ Alloys: An XAFS Study", *Phys. Rev.*, B50, 12401, (1994).
- R.A. Mayanovic, Q. Lu, B.A. Bunker, A.J. Kropf, and J.R. Buschert, "Glancing Angle XAFS and X-ray Reflectivity Study of Cu Thermal Vibration Amplitude at the $\text{Cu-Al}_2\text{O}_3$ Interface", *Physica*, B208, 405, (1995).
- J. McBreen, and S. Mukerjee, "In situ X-ray Absorption Studies of Pt-Ru Electrocatalyst", *J. Electrochem. Soc.*, 142, 3399, (1995).
- S. Mukerjee, J. McBreen, J.J. Reilly, J.R. Johnson, G. Adzic, K. Petrov, M.P.S. Kumar, W. Zhang, and S. Srinivasan, "In situ X-ray Absorption Spectroscopy Studies of Metal Hydride Electrodes", *J. Electrochem. Soc.*, 142, 2278, (1995).

M. Nicholson, and D.G. Nicholson, "Reduction of Copper(II) with Subsequent Disproportionation of Copper(I) During the Hydrothermal Syntheses of Microporous Silicoaluminium Phosphates SAPO⁻⁵ and ⁻¹¹", *J. Chem. Soc. Faraday Trans.*, 91, 3529, (1995).

K.I. Pandya, "Multiple-Scattering Effects in X-ray-Absorption Fine Structure: Chromium in a Tetrahedral Configuration", *Phys. Rev.*, B21, 15509, (1994).

K.I. Pandya, A. Russell, J. McBreen, and W.E. O'Grady, "EXAFS Investigations of Zn(II) in Concentrated Aqueous Hydroxide Solutions", *J. Of Phys. Chem.*, 99, 11967, (1995).

R.J. Reeder, G.M. Lambie, J.-F. Lee, and W.J. Staudt, "Mechanism of SeO₄²⁻ Substitution in Calcite: An XAFS Study", *Geochimica et Cosmochimica Acta*, 58, 5634, (1994).

A. Rubshtein, Y. Rosenberg, A. Frenkel, V. Manov, E. Veliyulin, A. Voronel, and E.A. Stern, "Structural, Thermal, and Electrical Properties of Al-Rich Metallic Glass", *Mat. Sci. Forum*, 179/181, 839, (1995).

D.L. Sullivan, R.D. Roark, J.G. Ekerdt, S. E. Deutsch, and B.C. Gates, "Reaction and Spectroscopic Study of Silica-Supported Molybdenum (IV) and Tungsten (IV) Dimers", *J. of Phys. Chem.*, 99, 3678, (1995).

N.D. Triantafyllou and B.C. Gates, "Magnesia-Supported Tetrairidium Clusters Derived From [Ir₄(CO)₁₂]", *J. of Phys. Chem.*, 98, 8431, (1994).

N.D. Triantafyllou, J.T. Miller, and B.C. Gates, "Iridium Clusters in KLTL Zeolite: Structure and Catalytic Selectivity for η -Hexane Aromatization", *J. of Catal.* 155, 131, (1995).

N.D. Triantafyllou, S.K. Purnell, C.J. Papile, J.-R. Chang, and B.C. Gates, "A Family of Rhenium Subcarbonyls on MgO: Structural Characterization by Extended X-ray Absorption Fine Structure Spectroscopy", *Langmuir*, 10, 4077, (1994).

Z. Xu, and B.C. Gates, "Cyclohexene Hydrogenation Catalyzed by MgO-supported Tetrairidium Clusters", *J. of Catal.*, 154, 335, (1995).

Z. Xu, F.-S. Xiao, S.K. Purnell, O. Alexeev, S. Kawi, S.E. Deutsch, and B.C. Gates, "Size-Dependent Catalytic Activity of Supported Metal Clusters", *Nature*, 372, 346, (1994).

Beamline X12C

J.-O. Lee, P. Rieu, M.A. Arnaout, and R. Liddington "Crystal Structure of the A Domain from the α Subunit of Integrin CR3 (CD11b/CD18)", *Cell*, 80, 631-638, (1995).

I. Schlichting, J. Berendzen, G.N. Phillips, Jr., and R.M. Sweet, "Crystal Structure of Photolyzed Carbonmonoxy Myoglobin", *Nature*, 371, 808-812, (1994).

R.-M. Xu, G. Carmel, R.M. Sweet, J. Kurek, and X. Cheng, "Crystal Structure of Casein Kinase-1, A Phosphate-Directed Protein Kinase", *The EMBO Journal*, 14, 1015-1023, (1995).

Beamline X14A

R.D. Aburano, H. Hong, J.M. Roesler, K. Chung, D.-S. Lin, P. Zschack, H. Chen, and T.-C. Chiang, "Boundary Structure Determination of Ag/Si(111) Interfaces by X-Ray Diffraction", *Phys. Rev.*, B52, 1839, (1995).

- R.D. Aburano, H. Hong, J.M. Roesler, D.-S. Lin, T.-C. Chiang, and P. Zschack, "X-Ray Study of the Ag/Si(111) Interface", *Surf. Sci. Lett.*, 339, L891, (1995).
- J. Cheng, S.C. Moss, M. Eisner, and P. Zschack, "X-Ray Characterization of Melanins I.", *Pigment Cell Research*, 7, 255, (1994).
- A. Goyal, E.D. Specht, D.M. Kroeger, T.A. Mason, D.J. Dingley, G.N. Riley, Jr., and M.W. Rupich, "Grain Boundary Misorientations and Percolative Current Paths in High-Jc Powder-in-Tube Bi-2223", *App. Phys. Lett.*, 66, 2903, (1995).
- A. Goyal, M. Paranthaman, Qing He, F.A. List, E.D. Specht, D.K. Christen, D.M. Kroeger, J.E. Tkaczyk, and P. Haldar, "Fabrication, Processing, and Properties of Tl-1223 Conductors", *IEEE Transactions in Applied Superconductivity*, 5, 1405, (1995).
- A. Goyal, E.D. Specht, D.M. Kroeger, D.K. Christen, J.E. Tkaczyk, J.A. DeLuca, and J.A. Sutliff, "Effect of the Colony Microstructure on Transport Critical Current of High-Jc Tl-1223 Thick Films", Proceedings of the 1995 International Workshop on Superconductivity co-sponsored by ISTE and MRS, p. 453, (1995).
- E.D. Isaacs, P. Zschack, A.P. Ramirez, C.S. Oglesby, and E. Bucher, "Antiferromagnetic Order in Superconducting UPt_3 : An X-Ray Magnetic Scattering Study", *J. Appl. Phys.*, 76, 6133, (1994).
- E.D. Isaacs, P. Zschack, C.L. Broholm, C. Burns, G. Aeppli, A.P. Ramirez, T.T.M. Palstra, E.W. Erwin, N. Stucheli, and E. Bucher, "Antiferromagnetism and its Relation to the Superconducting Phases of UPt_3 ", *Phys. Rev. Lett.*, 75, 1178, (1995).
- X. Jiang, G.E. Ice, C.J. Sparks, and P. Zschack, "Recovery of SRO Parameters and Pairwise Atomic Displacements in a $\text{Fe}_{46.5}\text{Ni}_{53.5}$ Alloy", *Mat. Res. Soc. Symp. Proc.*, 375, 267-273, (1995).
- V.M. Kaganer, I.R. Peterson, R.M. Kenn, M.C. Shih, M.K. Durbin and P. Dutta, "Tilted Phases of Fatty Acid Monolayers", *Chem. Phys. Lett.*, 102, 9412, (1995).
- D.M. Kroeger, A. Goyal, and E.D. Specht, "Paths for Current Flow in Polycrystalline High Temperature Superconductors", Proceedings of the 1995 International Workshop on Superconductivity Co-Sponsored by ISTE and MRS, p. 217, (1995).
- C.J. Sparks, G.E. Ice, X. Jiang, and P. Zschack, "Static Displacements of Atoms in Crystalline Metallic Solid Solutions", Applications of Synchrotron Radiation Techniques to Materials Science II, *Mat. Res. Soc. Proc.*, 375, 213, (1995).
- E.D. Specht, A. Goyal, D.M. Kroeger, J.A. DeLuca, J.E. Tkaczyk, C.L. Briant, and J.A. Sutliff, "The Effect of Colonies of Aligned Grains on Critical Current in High Temperature Superconductors", *Physica C*, 242, 164, (1995).
- J.Z. Tischler, J.D. Budai, D.E. Jesson, G. Eres, P. Zschack, J.M. Baribeau, and D.C. Houghton, "Ordered Structures in $\text{Si}_x\text{Ge}_{1-x}$ Alloy Thin-Films", *Phys. Rev.*, B51, 10947, (1995).
- J.E. Tkaczyk, J.A. Sutliff, J.A. DeLuca, P.J. Bednarczyk, C.L. Briant, Z.L. Wang, A. Goyal, D.M. Kroeger, D.H. Lowndes, and E.D. Specht, "Texture and Transport in Spray Pyrolyzed $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ Thick Films", *J. Mater. Res.*, 10, 2203, (1995).

Beamline X15A

E. Artacho, P. Molinàs-Mata, M. Böhrringer, G.E. Franklin, J.R. Patel, and J. Zegenhagen, "Microscopic Structure of the Discommensurate Phases in Ge(111)/Ga. I. Atomic Structure Within Domains", *Phys. Rev.*, B51, 9952, (1995).

G.E. Franklin, M.J. Bedzyk, J.C. Woicik, C. Liu, J.R. Patel, and J.A. Golovchenko, "Order-to-Disorder Phase Transition Study of Pb on Ge(111)", *Phys. Rev.*, B51, 2440, (1995).

G.E. Franklin, E. Fontes, Y. Qian, M.J. Bedzyk, J.A. Golovchenko, and J.R. Patel, "Thermal Vibration Amplitudes and Structure of As on Si(001)", *Phys. Rev.*, B50, 7483, (1994).

P.F. Lyman, Y. Qian, and M.J. Bedzyk, "Adsorbate Structure and Substrate Relaxation for the Sb/Si(100)-(2x1)", *Surf. Sci.*, 325, L385, (1995).

Y. Qian, and M.J. Bedzyk, "Structure and Ad-Atom Thermal Vibrational Amplitude of the Ga/Si(001) 2x1 Surface", *J. Vac. Sci. Tech.*, A13, 1613, (1995).

Y. Qian, N.C. Sturchio, R.P. Chiarello, P.F. Lyman, T.-L. Lee, and M.J. Bedzyk, "Lattice Location of Trace Elements Within Minerals and at Their Surfaces with X-ray Standing Waves", *Science*, 265, 1555, (1994).

S. Tang, A.J. Freeman, Y. Qian, G.E. Franklin, and M.J. Bedzyk, "Combined Theoretical and Experimental Investigations of the Adsorption Geometry of Ga on Si(100) at Low Coverage", *Phys. Rev.*, B51, 1593, (1995).

J. Wang, and M. Caffrey, "Locating Calcium in Membranes with X-ray Standing Waves", *J. Am. Chem. Soc.*, 117, 3304, (1995).

J.C. Woicik, G.E. Franklin, C. Liu, R.E. Martinez, I.-S. Hwang, M.J. Bedzyk, J.R. Patel, and J.A. Golovchenko, "Structural Determination of the Si(111) $\sqrt{3}\times\sqrt{3}$ -Bi Surface by X-ray Standing Waves and Scanning Tunneling Microscopy", *Phys. Rev.*, B50, 12246, (1994).

J. Zegenhagen, E. Artacho, P.E. Freeland, and J.R. Patel, "Surface Structures of Si(111)/Ga", *Phil. Mag.*, B70, 731, (1994).

J. Zegenhagen, T. Siegrist, E. Fontes, L.E. Berman, and J.R. Patel, "Epitaxy of Ultrathin Films of YBa₂Cu₃O₇ on Sr(001) Investigated With X-ray Standing Waves", *Solid State Commun.*, 93, 763, (1995).

Beamline X15B

L. E. Brus, P. F. Szajowski, W. L. Wilson, T. D. Harris, S. Schuppler, and P. H. Citrin, "Electronic Spectroscopy and Photophysics of Si Nanocrystals: Relationship to Bulk ϵ -Si and Porous Si", *J. Amer. Chem. Soc.*, 117, 2915-2922, (1995).

E. Özdas, A. R. Kortan, N. Kopylov, A. P. Ramirez, T. Siegrist, K. M. Rabe, H. E. Bair, S. Schuppler, and P. H. Citrin, "Superconductivity and Cation-Vacancy Ordering in the Rare-Earth Fulleride Yb_{2.75}C₆₀", *Nature*, 375, 126-129, (1995).

S. Schuppler, D.L. Adler, L.N. Pfeiffer, K.W. West, E.E. Chaban, and P.H. Citrin, "Identifying and Quantifying Point Defects Using X-ray Absorption Spectroscopy: Si-doped GaAs", *Phys. Rev.*, B51, 10527-10538, (1995).

S. Schuppler, S.L. Friedman, M.A. Marcus, D.L. Adler, Y.-H. Xie, F.M. Ross, T.D. Harris, W.L. Brown, Y.J. Chabal, L.E. Brus, E.E. Chaban, P.F. Szajowski, S.B. Christman, and P.H. Citrin, "Size, Shape, and Composition of Luminescent Species in Oxidized Si Nanoclusters and H-Passivated Porous Si", *Phys. Rev.*, B51, 10527, (1995).

S. Schuppler, S.L. Friedman, M.A. Marcus, D.L. Adler, Y.-H. Xie, F.M. Ross, T.D. Harris, W.L. Brown, Y.J. Chabal, P.F. Szajowski, E.E. Chaban, L.E. Brus, and P.H. Citrin, "X-ray Absorption Spectroscopy From Porous Si and Oxidized Si Nanocrystals", Applications of Synchrotron Radiation Techniques to Materials Science, edited by L.J. Terminello, N.D. Shinn, G.E. Ice, K.L. D'Amico, and D.L. Perry, *MRS Symp. Proc.*, 2, 375, (1995).

S. Schuppler, S. L. Friedman, M.A. Marcus, D.L. Adler, Y.-H. Xie, F.M. Ross, T.D. Harris, W.L. Brown, J.J. Chabal, P.F. Szajowski, E.E. Chaban, L.E. Brus, and P.H. Citrin, "Size, Shape, and Crystallinity of Luminescent Structures in Oxidized Si Nanoclusters, and H-Passivated Porous Si", Microcrystalline and Nanocrystalline Semiconductors, edited by R.W. Collins, C.C. Tsai, M. Hirose, F. Koch, and L.E. Brus, *MRS Symp. Proc.*, 358, (1995).

Y.-H. Xie, G.H. Gilmer, C. Roland, P.J. Silverman, S.K. Buratto, Y.J. Cheng, E.A. Fitzgerald, A.R. Kortan, S. Schuppler, M.A. Marcus, and P.H. Citrin, "Semiconductor Surface Roughness: Dependence on Sign and Magnitude of Bulk Strain", *Phys. Rev. Lett.*, 73, 3006-3009, (1994).

Y.-H. Xie, G. H. Gilmer, C. Roland, P. J. Silverman, S. K. Buratto, Y.J. Cheng, E. A. Fitzgerald, A. R. Kortan, S. Schuppler, M. A. Marcus, P. H. Citrin, "Step Energies and Roughening of Strained Layers - Reply", *Phys. Rev. Lett.* 74, 4963, (1995).

Beamline X16A

P.A. Bennett, M.Y. Lee, P. Yang, R. Schuster, P.J. Eng, and I.K. Robinson, "Template Structure at the Silicon/Amorphous-Silicide Interface", *Phys. Rev. Lett.*, 75, 2726, (1995).

J.L. Dawson, K. Krisch, K.W. Evans-Lutterodt, M.-T. Tang, L. Manchanda, M.L. Green, D. Brasen, G.S. Higashi, and T. Boone, "Kinetic Smoothing: Growth Thickness Dependence of The Interface Width of the Si(001)/SiO₂ Interface", *J. Appl. Phys.*, 77, 4746, (1995).

Evans-Lutterodt, and M.-T. Tang, "Angle Calculations for a 2+2 Surface X-ray Diffractometer", *J. Appl. Cryst.*, 28, 318, (1995).

H.L. Meyerheim, W. Moritz, H. Schulz, P.J. Eng, and I.K. Robinson, "Anharmonic Thermal Vibrations Observed by Surface X-ray Diffraction for Cs/Cu(001)", *Surf. Sci.*, 333, 1422, (1995).

S. Pflanz, H.L. Meyerheim, W. Moritz, I.K. Robinson, H. Hrnis, and E.H. Conrad, "The Anisotropic Roughing Transition of the Ag(110) Surface: X-ray Reflection Profile Analysis Using the Domain Matrix Method", *Phys. Rev.*, B52, 2914, (1995).

H. Reichert, P.J. Eng, H. Dosch, and I.K. Robinson, "Thermodynamics of Surface Segregation Profiles at Cu₃Au(001) Resolved by X-ray Scattering", *Phys. Rev. Lett.*, 74, 2006, (1995).

I.K. Robinson, P.J. Eng, and R. Schuster, "Origin of the Surface Sensitivity in Surface X-ray Diffraction", *Acta Phys. Polonica*, A86, 513, (1994).

R. Schuster, P.J. Eng, and I.K. Robinson, "Anomalous Coverage Behavior of the Cs-Ag Distance on Cs/Ag(110)", *Surf. Sci.*, 326, L477-L482, (1995).

Beamline X16B

E.D. Isaacs, P. Zschack, C.L. Broholm, C. Burns, G. Aeppli, A.P. Ramirez, T.T.M. Palstra, R.W. Erwin, N. Stucheli, and E. Bucher, "Antiferromagnetism and Its Relation to the Superconducting Phases in Upt_3 ", *Phys. Rev. Lett.*, 75, 1178, (1995).

Beamline X16C

K. Konstadinidis, R.L. Opila, M.A. Marcus, K. Short, A.E. White, A.O. Ibidunni, A. Davenport, and H. Isaacs, "X-ray Absorption Study of Ti and Cr Reactions with Triazine and Polyimide", *Mat. Res. Soc. Symp. Proc.*, 233, 345, (1994).

I.K. Robinson, H. Graafsma, A. Kvik, and J. Linderholm, "First Testing of the Fast Kappa Diffractometers at NSLS and ESRF", *Rev. Sci. Instrum.*, 66, 1765, (1995).

S.S. Sengupta, L. Ma, D.L. Adler, and D.A. Payne, "Extended X-ray Absorption Fine Structure Determination of Local Structure in Sol-gel-derived Lead Titanate, Lead Zirconate, and Lead Zirconate Titanate", *J. Mat. Res.*, 10, 1345, (1995)

K.L. Whiteaker, I.K. Robinson, C. Benson, D.M. Smilgies, N. Onda, and H. von Kaenel, "Disordered Structure of Cubic Iron Silicide Films on Si(111)", *Phys. Rev.*, B51, 9715, (1995).

Beamline X17B2

D. Chapman, W.C. Thomlinson, N.F. Gmür, J.P. Dervan, T. Stavola, J. Giacomini, H. Gordon, E. Rubenstein, W. Lavender, C. Schulze, and A.C. Thompson, "Effects of Spatial Resolution and Spectral Purity on Transvenous Coronary Angiography Images", *Rev. Sci. Instrum.*, 66/2, 1329-1331, (1995). BNL 60861

N.F. Gmür, D. Chapman, W. Thomlinson, A.C. Thompson, W.M. Lavender, K. Scalia, N. Malloy, J. Mangano and J. Jacob, "NSLS Transvenous Coronary Angiography Beamline Upgrade and Advanced Technology Initiatives", *Rev. Sci. Instrum.*, 66/2, 1357-1360, (1995). BNL 60857

C. Schulze, and D. Chapman, "PEPO: A Program for the Calculation of the Reflectivity of Cylindrically Bent Laue Crystal Monochromators", *Rev. Sci. Instrum.*, 66/2, 2220-2223, (1995). BNL 61689

Beamline X17C

T. S. Duffy, R. J. Hemley, and H. K. Mao, "Equation of State and Shear Strength at Multimegabar Pressures: Magnesium Oxide to 227 GPa", *Phys. Rev. Lett.*, 74, 1371-1374, (1995).

T. S. Duffy, C. Meade, Y. Fei, H. K. Mao, and R. J. Hemley, "High-Pressure Phase Transition in Brucite $\text{Mg}(\text{OH})_2$ ", *Am. Mineral.*, 80, 222-230, (1995).

Y. Fei, and H. K. Mao, "In situ Determination of the NiAs phase of FeO at High Pressure and High Temperature", *Science*, 266, 1678-1680, (1994).

Y. Fei, C. T. Prewitt, H. K. Mao, and C. M. Bertka, "Structure and Density of FeS at High Pressure and High Temperature and the Internal Structure of Mars", *Science*, 268, 1892-1894, (1995).

G. Gu, Y.K. Vohra, J.M. Winand, and J.C. Spirlet, "Pressure-Concentration (P-X) Diagram for the Ce-Th Alloy System", *Scripta Metallurgica et Materialia*, 32, 2081, (1995).

R. J. Hemley, and H. K. Mao, "Progress on Hydrogen at Ultrahigh Pressures", in Oji Seminar Volume: Elementary Processes in Dense Plasmas, edited by S. Ichimaru, and S. Ogata, Addison-Wesley Pub. Co., Tokyo, pp. 271-282, (1995).

R. J. Hemley, H. K. Mao, T. S. Duffy, J. H. Eggert, A. F. Goncharov, M. Hanfland, M. Li, M. Somayazulu, W. Vos, and C. S. Zha, "Dense Hydrogen in the Outer Solar System: Implications from Recent High-Pressure Experiments", in Volatiles in the Earth and Solar System, edited by K. A. Farley, Am. Inst. Physics, New York, pp. 250-260, (1995).

C. C. Kim, A. R. Drews, E. F. Skelton, S. B. Qadri, M. S. Osofsky, M. E. Reeves, and D. H. Liebenberg, "Volume Dependence of the Superconducting Transition Temperature for the High Temperature Superconductor $\text{HgBa}_2\text{Ca}_{2-x}\text{Pb}_x\text{Cu}_3\text{O}_{8+\delta}$ ", *Phys. Rev.*, B50/18, 13778, (1994).

K. J. Kingma, R. J. Hemley, H. K. Mao, and D. R. Veblen, Reply to McNeil and Grimsditch's Comment on "New High-Pressure Transformation in α -Quartz", *Phys. Rev. Lett.*, 72, 1302, (1994).

H. K. Mao, "Pressure Alchemy", *Rev. High Pressure Sci. Tech.-Japanese High-Pressure Soc.*, 3, 8-11, (1994).

H. K. Mao, R. J. Hemley, and A. L. Mao, "Recent Design of Ultrahigh-Pressure Diamond Cell", in High Pressure Science and Technology-1993, edited by S. C. Schmidt, J. W. Shaner, G. A. Samara, and M. Ross, AIP Press, New York, 2, pp. 1613-1616, (1994).

C. Meade, H. K. Mao, and J. Hu, "High-Temperature Phase Transition and Dissociation of $(\text{Mg,Fe})\text{SiO}_3$ Perovskite at Lower Mantle Pressures", *Science*, 268, 1743-1745, (1995).

E. F. Skelton, S. B. Qadri, M. S. Osofsky, A. R. Drews, P. R. Broussard, J. Z. Hu, L. W. Finger, T. A. Vanderah, D. Kaiser, J. L. Peng, S. A. Anlage, R. L. Greene, J. Giapintzakis, and D. M. Ginsberg, "Direct Observation of Microscopic Inhomogeneities in High T_c Superconductors", *SPIE Proc.*, 2516, (1995).

Y. K. Vohra, T.S. McCauley, and S.S. Vagarali, "Applications of Isopure and Natural Abundance Synthetic Diamonds in High Pressure Research", in Advances in New Diamond Science and Technology, edited by S. Saito, N. Fujimori, O. Fukunaga, M. Kamo, K. Kobashi, and M. Yoshikawa, MYU, Tokyo, p. 391, (1994).

Beamline X18A

J.B. Cohen, "Long-Range Ordering in the Early Stages of Precipitation-A Brief Review", *Metallurgical and Materials Transactions A*, 25A, 2564-68, (1994).

R. Colella, "Enantiomorphism and Multiple Beam Diffraction. Revised", *Acta Cryst.*, A51, 438, (1995).

R. Colella, Multiple Bragg Scattering and the Phase Problem in X-ray Diffraction. I Perfect Crystals", *Comments Cond. Matt. Phys.*, 17, 175, (1995).

R. Colella, "Multiple Bragg Scattering and the Phase Problem in X-ray Diffraction. II Mosaic Crystals", *Comments Cond. Matt. Phys.*, 17, 199, (1995).

K.W. Herwig, B. Matthies, and H. Taub, "Preparation of Long-alkane Monolayers Adsorbed on Exfoliated Graphite for Neutron Diffraction Studies", Neutron Scattering in Materials Science, edited by D.A. Nuemann, T.P. Russell, and B.J. Wuensch, *Mater. Res. Soc. Symp. Proc.*, 376, (1994).

K.W. Herwig, J.C. Newton, and H. Taub, "Structure and Growth of Butane Films Adsorbed on Graphite", *Phys. Rev.*, B50, 15287-15297, (1994).

X.B. Kan, H. Renevier, J. Quintana, J.L. Peng, and J.B. Cohen, "Anomalous X-ray Diffuse Scattering Study of Short-Range Order in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ", *J. App. Phys.*, 77/1, 34-40, (1995).

S. Mansour, G. Liedl, and R. Vest, "Microstructural Developments and Dielectric Properties of Rapid Thermally Processed PZT Thin Films Derived by Metallo-Organic Decomposition", *J. Am. Ceram. Soc.*, 78/6, 1617-23, (1995).

J.L. Parrill, J.B. Cohen, and Y.-W. Chung, "Ultra-High Vacuum Grazing Incidence Small Angle X-ray Scattering Camera for *in situ* Surface Analysis", *Advances in X-ray Analysis*, edited by J.V. Gilfrich, et al., 37, 413-418, (1994).

H. Renevier, X.B. Kan, J.P. Quintana, K.J. Zhang, and J.B. Cohen, "Local Order in $\text{Yb}_{2-x}\text{Cu}_{3-y}\text{Co}_y\text{O}_{6+2x}$ Studied by Anomalous Diffuse X-ray Scattering", *J. Mat. Res.*, 9/12, 3050-58, (1994).

N. Takesue, M. Maglione, and H. Chen, "X-ray Thermal-Diffuse-Scattering (TDS) Study of Soft Modes in Paraelectric BaTiO_3 ", *Phys. Rev. Lett.*, 51/10, 6696-6699, (1994).

C. Venkatraman and G.L. Liedl, "Oriented Texture in $\text{Yb}_{2-x}\text{Cu}_3\text{O}_{7.8}$ Films Synthesized From Amorphous Precursors", *J. Of Electr. Mat.*, 23, 11, (1994).

H. Zhang, H. Sato, and G.L. Liedl, Possible Effect of Oxygen Content on the Under-Doped Characteristics of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\delta}$ Compound", *Physica*, C234, 185-89, (1994).

Beamline X18B

D.-J. Liu, and H.J. Robota, "In situ Characterization of Cu-ZSM-5 by X-Ray Absorption Spectroscopy: XANES Study of Cu Oxidation State in Cu-ZSM-5 During the Selective Catalytic Reduction of NO by Hydrocarbons", *Appl. Catal.*, B4, 155, (1994).

Beamline X19A

M.R. Antonio, and L. Soderholm, "Cerium Valence in Cerium-Exchanged Preyssler's Heteropolyanion Through X-ray Absorption Near-Edge Structure", *Inorg. Chem.*, 33, 5988-5993, (1994).

M.J. Baldwin, T.L. Stemmler, P.J. Riggs-Gelasco, M.L. Kirk, J.E. Penner-Hahn, and V.L. Pecoraro, "Structural and Magnetic Effects of Successive Protonations of Oxo Bridges in High Valent Manganese Dimers", *J. Am. Chem. Soc.*, 116, 11349-11356, (1994)

L.J. Blanchard, J.D. Robertson, S. Srikantapura, B.K. Parekh, and F.E. Huggins, "Potentially Hazardous Trace Elements in Kentucky Coals", *ACS Div. Fuel Chem.*, 40, 828-833, (1995).

C. Bouldin, L. Furenlid, and T. Elam, "MacXAFS: An EXAFS Analysis Package for the Macintosh", *Physica*, B208/209, 190-192, (1995).

M.-I. M. Chou, J.M. Lytle, Y.C. Li, F.E. Huggins, G.P. Huffman, and K.K. Ho, "Chlorine in Five Illinois Coals and Three British Coals: An X-ray Absorption Near-Edge Structure (XANES) Spectroscopy Investigation", *ACS Div. Fuel Chem.*, 40, 402-406, (1995).

M.-I. M. Chou, W.P. Pan, F.E. Huggins, J.M. Lytle, L. Liu, G.P. Huffman, and K.K. Ho, "Chlorine in Coal and Boiler Corrosion", *Proceedings, Eleventh Annual Pittsburgh Coal Conference*, Pittsburgh Energy Technology Center (U.S. DOE), Pittsburgh, PA, pp. 359-364, (1994).

- A.J. Davenport, J.A. Bardwell, and C.M. Vitus, "In Situ XANES Study of Galvanostatic Reduction of the Passive Film on Iron", *J. Electrochem. Soc.*, 142/3, 721-724, (1995).
- T.I. Eglinton, J.E. Irvine, A. Vairavamurthy, W. Zhou, and B. Manowitz, "Formation and Diagenesis of Macromolecular Organic Sulfur in Peru Margin Sediments", *Organic Geochemistry*, 22, 781-799, (1994).
- L.R. Furenlid, M.W. Renner, and E. Fujita, "XAS Studies of Ni(I), Ni(II), and Ni(III) Complexes", *Physica*, B208-209, 739-742, (1994).
- H. Hu, I.E. Wachs, and S.R. Bare, "Surface Structure of Supported Molybdenum Oxide Catalysts: Characterization by Raman and Mo L₃-edge XANES", *J. Phys. Chem.*, 99, 10897, (1995).
- G.P. Huffman, F.E. Huggins, N. Shah, F. Lu, and J. Zhao, "XAFS Studies of Coal", *ACS Div. Fuel Chem.*, 39, 77-80, (1994).
- G.P. Huffman, N. Shah, F.E. Huggins, L.M. Stock, K. Chatterjee, J.J. Kilbane, II, M.-I. M. Chou, and D.H. Buchanan, "Sulfur Speciation of Desulfurized Coals by XANES Spectroscopy", *Fuel*, 74, 549-555, (1995).
- G.P. Huffman, N. Shah, J. Zhao, F.E. Huggins, T.E. Hoost, S. Halvorsen, and J.E. Goodwin, Jr., "In situ XAFS Investigation of K-Promoted Co Catalysts", *J. Catalysis*, 151, 17-25, (1995).
- F.E. Huggins, and G.P. Huffman, "Chlorine in Coal: An XAFS Spectroscopic Investigation", *Fuel*, 74, 556-569, (1995).
- F.E. Huggins, B.K. Parekh, J.D. Robertson, and G.P. Huffman, "Modes of Occurrence of Trace Elements in Coal: Geochemical Constraints from XAFS and PIXE Spectroscopic Analysis of Advanced Coal Cleaning Tests", International Conference on Coal Science (Oviedo, Spain), Conference Proceedings, Elsevier, Amsterdam, pp. 175-180, (1995).
- F.E. Huggins, M.M. Taghiei, and G.P. Huffman, "XAFS Spectroscopic Investigation of Element Speciation in Carbonaceous Materials From Coliquiefaction of Coals and Waste Materials", Book of Abstracts , Emerging Technologies in Hazardous Waste Management VI, edited by D.W. Tedder, *American Chemical Society*, Vol. II, pp. 993-996, (1994).
- F.E. Huggins, J. Zhao, N. Shah, and G.P. Huffman, "Modes of Occurrence of Trace Elements in Coal From XAFS Spectroscopy", *ACS Div. Fuel Chem.*, 39, 504-510, (1994).
- G. Liang, R. Barber, Y. Tang, M. Croft, J. Cobb, and J.T. Markert, "Transition from a Mixed-Valent System to a Magnetically Ordered Kondo Lattice in Ce(NiSi)_{2-x}(CuGe)_x", *Phys. Rev.*, B51, 214, (1995).
- G. Liang, Y. Guo, W. Xu, D. Badresingh, J. Chen, A. Sahiner, M. Croft, O. Beom-hoan, and J.T. Markert, "X-Ray Absorption Studies of Electron Doping and Band Shifts in R_{2-x}Ce₂CuO_{4-δ} (R=Pr, Nd, Sm, Eu, Gd)", *Phys. Rev.*, B51, 1258, (1995).
- J. Liu, Y. Gagnon, J. Gauthier, L. Furenlid, P. L'Heureux, M. Auger, O. Nureki, S. Yokoyama, and J. Lapointe, "The Zinc-Binding Site of *Escherichia coli* Glutamyl-tRNA Synthetase is Located in the Acceptor-Binding Domain", *J. Biol. Chem.*, 270, 15162-15169, (1995).
- M. Najih, F.E. Huggins, and G.P. Huffman, "Determination of Chromium Oxidation States in Coal Combustion Products by XAFS Spectroscopy", *ACS Div. Fuel Chem.*, 40, 808-812, (1995).

R. Nitsche, M. Winterer, M. Croft, and H. Hahn, "EXAFS Study on Nanostructured Zirconia and Ytria", *Nucl. Instrum. and Meth.*, B97, 127-132, (1995).

D.M. Pfund, J.G. Darab., J.L. Fulton, and Y. Ma, "An XAFS Study of Strontium Ions and Krypton in Supercritical Water", *J. Phys. Chem.*, 98, 13102-13107, (1994).

M.W. Renner, L.R. Furenlid, and A.M. Stolzenberg, "Effects of Metal-Centered Reduction on the Structural, Electronic, and Coordination Properties of Nickel and Copper Octaethylisobacteriochlorins", *J. Am. Chem. Soc.*, 117, 293-300, (1995).

P.J. Riggs-Gelasco, Structural Characterization of the Manganese Cluster of the Oxygen Evolving Complex of Photosystem II Using X-ray Absorption Spectroscopy, PhD. Thesis, Advised by J.E. Penner-Hahn, University of Michigan, (1994).

A. Sahiner, M. Croft, S. Gua, I. Perez, Z. Zhang, M. Greenblatt, P. Metcalf, H. Johns, and G. Liang, "Polarized XAS Studies of Ternary Nickel Oxides", *Phys. Rev.*, B51, 5879, (1995).

S. Shah, A. Ward, and A.J. Davenport, "Characterization of Tellurium-Based Conversion Coatings by X-Ray Absorption Near-Edge Structure and Fourier Transform Infrared Spectroscopy", *Corrosion*, 51/1, 67-70, (1995).

N. Shah, J. Zhao, K.R.P.M. Rao, F.E. Huggins, and G.P. Huffman, "*In situ* XAFS Spectroscopic Studies of DCL Catalysts", International Conference on Coal Science (Oviedo, Spain), Elsevier, Amsterdam, pp. 1279-1284, (1995).

D.L. Tierney, J.A. Fee, M.L. Ludwig, and J.E. Penner-Hahn, "X-Ray Absorption Spectroscopy of the Iron Site in *E. Coli* Fe(III) Superoxide Dismutase", *Biochemistry*, 34, 1661-1668, (1995).

A. Vairavamurthy, W. Zhou, E. Eglinton, and B. Manowitz, "Sulfonates: a Novel Class of Organic Sulfur Compounds in Marine Sediments", *Geochimica et Cosmochimica Acta*, 58, 4681-4687, (1994).

A. Vairavamurthy, B. Manowitz, W. Zhou, and Y. Jeon, "Determination of Hydrogen-sulfide Oxidation Products by Sulfur K-edge XANES Spectroscopy", The Environmental Geochemistry of Sulfide Oxidation, edited by C. Alpers and D. Blowes, American Chemical Society, Washington, DC, 505, pp. 412-30, (1994).

G.S. Waldo, and J.E. Penner-Hahn, "The Mechanism of Mn Catalase Peroxide Disproportionation: Determination of Mn Oxidation States During Turnover", *Biochemistry*, 34, 1507-1512, (1995).

R.T. Witkowski, S. Hattman, L. Newman, K. Clark, D.L. Tierney, J.E. Penner-Hahn, and G. McLendon, "The Zinc Coordination Site of the Bacteriophage Mu Translational Activator Protein, Com", *J. Mol. Biol.*, 247, pp. 753-64, (1995).

J. Zhao, Z. Feng, F.E. Huggins, N. Shah, G.P. Huffman, and I. Wender, "Role of Molybdenum at the Iron Oxide Surface", *J. Catalysis*, 148, 194-197, (1994).

J. Zhao, F.E. Huggins, Z. Feng, and G.P. Huffman, "Ferrihydrite: Surface Structure and Its Effects on Phase Transformation", *Clays and Clay Minerals*, 42, 737-746, (1994).

Z. Zhu, Y. Gu, S.C. George, M.A. Wilson, F.E. Huggins, and G.P. Huffman, "A Study of Sulphur and Nitrogen in Two High Sulphur Coals", International Conference on Coal Science (Oviedo, Spain), Elsevier, Amsterdam, pp. 1681-1686, (1995).

Beamline X19C

I. Baker, and F. Liu, "An *in situ* Study of Dislocation/Grain Boundary Interactions Using X-ray Topography and TEM", in Defect-Interface Interactions, edited by E.P. Kvam, A.H. King, M.J. Mills, T.D. Sands, and V. Vitek, Mat. Res. Soc. Symp. Proc., p. 319, (1994).

H. Chung, B. Raghotamachar, J. Wu, M. Dudley, D.J. Larson, Jr., and D.C. Gillies, "Characterization of Growth Defects in CdZnTe Single Crystals by Synchrotron White Beam X-ray Topography", in Defect and Impurity-Engineered Semiconductors and Devices, edited by S. Ahok, J. Chevallier, I. Akasaki, N.M. Johnson, and B.L. Sopori, Mat. Res. Soc. Symp. Proc., 378, 41, (1995).

D. DiMarzio, D.J. Larson, Jr., L.G. Casagrande, J. Wu, M. Dudley, and P.-K. Liao, "Defect Mapping of CdZnTe Substrates", in Proceedings of the 1993 IRIS Specialty Group on Infrared Materials, (August 16-17, 1993), ERIM, Ann Arbor, MI, p. 69, (1994).

M. Dudley, W. Huang, S. Wang, J.A. Powell, P. Neudeck, and C. Fazi, "White Beam Synchrotron Topographic Analysis of Multipolytype SiC Device Configurations", J. Phys. D. Appl. Phys., 28, A56, (1994).

M. Dudley, S. Wang, W. Huang, C.H. Carter, Jr., and C. Fazi, "White Beam Synchrotron Topographic Studies of Defects in 6H-SiC Single Crystals", J. Phys. D. Appl. Phys., 28, A63, (1994).

Z. Huang, M.L. Schlossman, A.A. Acero, Z. Zhang, N. Lei, and S.A. Rice, "Thermal Expansion Coefficient of a Water-Supported Perfluoro-n-Eicosane Monolayer", Langmuir, 11, 2742, (1995).

W. Huang, S. Wang, M. Dudley, P. Neudeck, J.A. Powell, and C. Fazi, "Computer Aided Synchrotron White Beam X-ray Topographic Analysis of Multipolytype SiC Device Configurations", in Applications of Synchrotron Radiation Techniques to Materials Science, edited by L. Terminello, N. Shinn, G. Ice, K. D'Amico, and D. Perry, Mat. Res. Soc. Symp. Proc., 375, 327, (1995).

F. Liu, I. Baker, and M. Dudley, "A New Method to Characterize Dislocations Loops", in Applications of Synchrotron Radiation Techniques to Materials Science, edited by L. Terminello, N. Shinn, G. Ice, K. D'Amico, and D. Perry, Mat. Res. Soc. Symp. Proc., 375, 319, (1995).

F. Liu, and I. Baker, "Synchrotron X-ray Topographic Studies of Grain Boundaries", Microscopy Society of American Bulletin, 24, 351, (1994).

S.P. Tobin, F.T.J. Smith, P.W. Norton, J. Wu, M. Dudley, D. DiMarzio, and L. Casagrande, "The Relationship Between Lattice Matching and Crosshatch in LPE HgCdTe on CdZnTe Substrates", J. Elect. Mat., 24, 1189, (1995).

S. Wang, M. Dudley, C.H. Carter, Jr., V.F. Tsvetkov, and C. Fazi, "Synchrotron White Beam Topography Studies of Screw Dislocations in 6H-SiC Single Crystals", in Applications of Synchrotron Radiation Techniques to Materials Science, edited by L. Terminello, N. Shinn, G. Ice, K. D'Amico, and D. Perry, Mat. Res. Soc. Symp. Proc., 375, 281, (1995).

S. Wang, M. Dudley, W. Huang, C.H. Carter, Jr., V.F. Tsvetkov, and C. Fazi, "Characterization of Defects in Silicon Carbide Single Crystals by Synchrotron X-ray Topography", in Proceedings of International Workshop on Semiconductor Characterization: Present Status and Future Needs, edited by W. Murray Bullis, David G. Seiler, and Alain Diebold, American Institute of Physics, p. 278, (1995).

Beamlines X20A, X20B, & X20C

R.J.Birgeneau, Q.Feng, Q.J.Harris, J.P.Hill, A.P.Ramirez and T.R.Thurston, "X-Ray, Neutron Scattering, Magnetization, and Heat Capacity Study of the 3D Random Field Ising Model", *Phys. Rev. Lett.*, 75, 1198, (1995).

J.D. Brock, A.C. Finnefrock, K.L. Ringland, and E. Sweetland, "Detailed Structure of CDW in a Quenched Random Field", *Phys. Rev. Lett.*, 73, 3588, (1994).

C. Cabral, Jr., L.A. Clevenger, G.B. Stephenson, S. Brauer, G.Morales and K. Ludwig, Jr., "In Situ X-ray Diffraction and Resistivity Analysis of CoSi₂ Phase Formation With and Without A Ti Interlayer at Rapid Thermal Annealing Rates", *Mat. Res. Symp. Proc.*, 375, 253, (1994).

L. Clevenger, R.A. Roy, C. Cabral, Jr., K.L. Saenger, S. Brauer, G. Morales, K.F. Ludwig, Jr., G. Gifford, J. Bucchignano, J. Jordan-Sweet, P. DeHaven, and G.B. Stephenson, "An *in situ* Study of C54-TiSi₂ Formation in Submicron Salicide and Polycide Structures", *J. Mater. Res.*, 10, 2355, (1995).

B.J. Factor, T.P. Russell, and M.F. Toney, "The Near Surface Structure of Aromatic Polyimides: The Effect of Precursor Isomers", *Faraday Disc.*, 98, 319, (1995).

R.F.C. Farrow, R.F. Marks, G.R. Harp, D. Weller, T.A. Rabedeau, M.F. Toney, and S.S.P. Parkin, "MBE Growth of Artificially-Layered Magnetic Metal Structures", in Molecular Beam Epitaxy: Applications to Key Materials, edited by R.F.C. Farrow, Noyes, New York, p. 623-744, (1995).

J.G. Gordon, O.R. Melroy, and M.F. Toney, "Structure of Metal-Electrolyte Interfaces: Copper on Gold(111) & Water on Silver(111)", *Electrochim Acta*, 40, 3, (1995).

Q.J. Harris, Q. Feng, R.J. Birgeneau, K. Hirota, K. Kakurai, J.E. Lorenzo, G. Shirane, M. Hase, K. Uchinokura, H. Kojima, I. Tanaka, and Y. Shibuya, "Thermal Contraction at the Spin-Peierls Transition in CuGeO₃", *Phys. Rev.*, B50, 12606, (1994).

Q.J. Harris, D.Y. Noh, D.A. Turnbull, and R.J. Birgeneau, "Hexatic Order in Thin Smectic F Liquid Crystal Films", *Phys. Rev. E*, 51, 5795, (1995).

G.A. Held, and J.D. Brock, "Calculation of X-Ray Diffraction Profiles from Vicinal Surfaces", *Phys. Rev.*, B51, 7262, (1995).

G.A. Held, D.M. Goodstein, and J.D. Brock, "Phase Separation and Step Roughening of Vicinal Si(111): An X-Ray Scattering Study", *Phys. Rev.*, B51, 7269, (1995).

J.L. Jordan-Sweet, P.M. Mooney, and G.B. Stephenson, "High Resolution X-Ray Diffraction Measurements of Graded SiGe Multilayer Structures", Applications of Synchrotron Radiation Techniques to Materials Science II, *Mat. Res. Soc. Symp. Proc.* 375, 201, (1995).

P.M. Mooney, F.K. LeGoues, and J.L. Jordan-Sweet, "Dislocation Nucleation Barrier in SiGe/Si Structures Graded to Pure Ge", *Appl. Phys. Lett.*, 65, 2845, (1994).

P.M. Mooney, J.L. Jordan-Sweet, J.O. Chu, and F.K. LeGoues, "Evolution of Strain Relaxation in Step-Graded SiGe/Si Structures", *Appl. Phys. Lett.*, 66/26, 3642, (1995).

W.J. Nuttall, D.Y. Noh, B.O. Wells, and R.J. Birgeneau, "Isothermal Melting of Near-Monolayer Xenon on Single-Crystal Graphite", *J. Phys. Condens. Matter*, 7, 4337-4350, (1995).

R.A. Roy, L.A. Clevenger, C. Cabral, Jr., K.L. Saenger, G.B. Stephenson, S. Brauer, J.L. Jordan-Sweet, J. Bucchigano, G. Morales, and K.F. Ludwig, Jr., "In Situ X-ray Diffraction Analysis of C49-C54 Titanium Silicide Phase Formation in Narrow Lines", *Appl. Phys. Lett.*, 66/14, 1732, (1995).

S. Song, and S. G. J. Mochrie, "Attractive Step-Step Interaction, Tricriticality, and Faceting in the Orientational Phase Diagram of Silicon Surfaces Between [113] and [114]", *Phys. Rev.*, B51,10068, (1995).

S. Song, M. Yoon, and S. G. J. Mochrie, "Faceting, Tricriticality, and Attractive Interactions Between Steps in the Orientational Phase Diagram of Silicon Surfaces Between [113] and [5512]" *Surf. Sci.*, 334, 153, (1995).

S. Song, S. G. J. Mochrie, and G. B. Stephenson, "Faceting Kinetics of Stepped Si(113) Surfaces: A Time-Resolved X-Ray Scattering Study", *Phys. Rev. Lett.*, 74, 5240, (1995).

M.F. Toney, T.P. Russell, J.A. Logan, H. Kikuchi, J.M. Sands, and S.K. Kumar, "Near-Surface Alignment of Polymers in Rubbed Films", *Nature*, 374, 709, (1995).

M.F. Toney, J.G. Gordon, M.G. Samant, G.L. Borges, O.R. Melroy, D.Yee, and L.B. Sorensen, "The *In situ* Atomic Structure of Underpotentially Deposited Monolayers of Pb and Tl on Au(111) and Ag(111): A Surface X-Ray Scattering Study", *J. Phys. Chem.*, 99, 4733, (1995).

M. Yoon, S. G. J. Mochrie, D. M. Zehner, G. M. Watson, and Doon Gibbs, "Periodic Step-bunching on a Miscut Pt(111) Surface", *Surf. Sci.*, 338, 225, (1995).

Beamline X21

K. Hamalainen, M. Kirsch, F. Sette, C.-C. Kao, W. Caliebe, and J.B. Hastings, "A High Resolution X-ray Spectrometer Based on a Cylindrically Bent Crystal in Non-Dispersive Geometry", *Rev. Sci. Instrum.*, 66, 1525, (1995).

C.-C. Kao, K. Hamalainen, M. Kirsch, D.P. Siddons, T. Overslizen, and J.B. Hastings, "Optical Design and Performance of the Inelastic Scattering Beamline at the National Synchrotron Light Source", *Rev. Sci. Instrum.*, 66, 1699, (1995).

M.H. Kirsch, C.-C. Kao, F. Sette, W.A. Caliebe, K. Hamalainen, and J.B. Hasting, "Evidence for Quadrupolar Contribution to the Absorption Cross Section at the LIII Edge of Gadolinium in Gadolinium Gallium Garnet", *Phys. Rev. Lett.*, 74, 4931, (1995).

A.T. Macrander, V.I. Kushnir, and R.C. Bladell, "Performance of Spherically Focusing Ge(444) Backscattering Analyzers for Inelastic X-ray Scattering", *Rev. Sci. Instrum.*, 66, 1546, (1995).

Beamline X22B

R. R. Adzic, J. Wang, and B.M. Ocko, "Structure of Metal Adlayers During The Course of Electrocatalytic Reactions: O₂ Reduction on Au(111) With TI Adlayers in Acid Solution", *Electrochimica Acta*, 40, 83-89, (1995)

M. Deutsch, X.Z. Wu, E.B. Sirota, S.K. Sinha, B.M. Ocko, and O.M. Magnussen, "Crystalline Bilayers on the Surface of Molten Alcohol", *Europhys. Lett.*, 30, 283-288, (1995).

W.J. Foster, Jr., X-ray Optical Studies of Thin Organic Films, PhD.Thesis, Harvard University, June, 1995.

W.J. Foster, M.C. Shih, and P.S. Pershan, "The Structure and Phases of a Relaxed Langmuir Monolayer of Methyl Eicosanoate as Determined by Grazing Incidence X-ray Diffraction and Brewster Angle Microscopy", Proc. Of

Materials Research Society, Symposium AA: Applications of Synchrotron Radiation Techniques to Materials Science II, Boston, MA, edited by D.L. Perry, G. Ice, N. Shinn, K. D'Amico and L. Terminello, p. 187, (1995).

A. Gibaud, D.F. McMorro, and P.P. Swaddling, "Determination of the X-ray Scattering Lineshape From a Nb Film Using Synchrotron Radiation", *J. Phys. Chem.*, 7, 2645-54, (1995).

G.S. Kellog, P.S. Pershan, E.H. Kawamoto, W. Foster, M. Deutsch, and B.M. Ocko, "X-ray Reflectivity Measurements and Landau Theory of Smectic Wetting in nCB/Benzyl Alcohol Mixtures", *Phys. Rev.*, E51, 4709, (1995).

S.D. Kosowsky, C.H. Hsu, P.S. Pershan, J. Bevk, and B.S. Freer, "X-ray Scattering Studies of SiO/Si/Ge(001)", *Appl. Surf. Sci.*, 84, 179, (1995).

O.M. Magnussen, B.M. Ocko, R.R. Adzic, and J. Wang, "X-ray Diffraction Studies of Ordered Chloride and Bromide Monolayers at the Au(111)-Solution Interface", *Phys. Rev.*, B51, 5510-5513, (1995).

O.M. Magnussen, B.M. Ocko, M.J. Regan, K. Penanen, P.S. Pershan, and M. Deutsch, "X-ray Reflectivity Measurements of Surface Layering in Liquid Mercury", *Phys. Rev. Lett.* 74, 4444, (1995).

B.M. Ocko, O.M. Magnussen, R.R. Adzic, J. Wang, Z. Shi, Z. and J. Lipkowski, "A Critical Comparison of Electrochemical and Surface X-ray Scattering Results at the Au(111) Electrode in KBr Solutions", *J. Electroanal. Chem.*, 376, 35-39, (1994).

W. Polewska, J.X. Wang, B.M. Ocko, and R.R. Adzic, "Scanning Tunneling Microscopy Studies of Electrodeposited Thallium Monolayers on Au(111) in Alkaline Solution and a Comparison With Surface X-ray Scattering Data", *J. Electroanal. Chem.*, 376, 41-48, (1994).

J.P. Rieu, J.F. Legrand, A. Renault, B. Berge, B.M. Ocko, X.Z. Wu, and M. Deutsch, "Melting of 1-alcohol Monolayers at the Air-Water Interface. I) X-ray Reflectivity Investigations", *J. Phys. II*, 5, 607-619, (1995).

E. Smela, and L.J. Martinez Miranda, "Effect of Substrate Preparation on Smectic Liquid-Crystal Alignment .2. Further Results and Modeling", *J. Of Appl. Phys.*, 77, 1923-1929, (1995).

E. Smela, and L.J. Martinez Miranda, "Effect of Substrate Preparation on Smectic Liquid-Crystal Alignment .3. The Significance of Thermal History", *J. Of Appl. Phys.*, 77, 1930-1933, (1995).

P. Sonntag, P. Bodeker, K. Brohl, T. Thurston, and H. Zabel, "Charge-Density Waves and Strain Waves in Thin Epitaxial Cr Films", *Nucl. Instrum. And Meth. In Phys. Res.*, 97, 468-471, (1995).

Beamline X22C

N. Bernhoeft, A. Stunault, C. Vettier, F. de Bergevin, D. Gibbs, T.R. Thurston, S.M. Shapiro, J.B. Hastings, P. Dalmas, G. Helgesen, and O. Vogt, "Antiferromagnetic Layer Formation in UAs", *J. Magn. and Magn. Mater.*, 140/144, 1421-1422, (1995).

J.P. Hill, G. Helgesen, and D. Gibbs, "X-ray Scattering Study of Charge- and Spin-Density Waves in Chromium", *Phys. Rev.*, B51, 10336-10344, (1995)

G.H. Lander, W.G. Stirling, S. Landridge, and D. Gibbs, "Resonant X-ray Scattering in 5f Magnetism", *J. Magn. Mater.*, 140/144, 1349-1352, (1995).

G.H. Lander, W.G. Stirling, S. Landridge, C.C. Tand, and D. Gibbs, "Resonant Magnetic X-ray Scattering: a New Probe for Actinides", *J. Of Alloys & Compounds*, 213/214, 114, (1994).

S. Langridge, W.G. Stirling, G.H. Lander, and J. Rebizant, "Resonant Magnetic X-ray Scattering Studies of NpAs. I. Magnetic and Lattice Structure", *Phys. Rev.*, B49, 12010, (1994).

S. Landridge, W.G. Stirling, G.H. Lander, and J. Rebizant, "Resonant Magnetic X-ray Scattering Studies of NpAs. II. The Critical Regime", *Phys. Rev.*, B49, 12022, (1994).

C.F. Majkrzak, J.F. Ankner, N.F. Berk, and D. Gibbs, "Neutron and X-ray Diffraction Studies of Magnetic Multilayers", *Magnetic Multilayers*, edited by R.E. Watson and L.H. Bennett, World Scientific Pub., pp. 299-354, (1994).

D.F. McMorow, J.A. Simpson, R.A. Cowley, D.A. Jehan, R.C.C. Ward, M.R. Wells, T.R. Thurston, and D. Gibbs, "The Magnetic Structure of Holmium-Erbium Superlattices", *J. Magn. and Magn. Mater.*, 140/144, 1550-1553, (1995).

W.J. Nuttall, S. Langridge, W.G. Stirling, G.H. Lander, B. Lebech, D. Gibbs, and O. Vogt, "Resonant X-ray and Neutron Diffraction Study of $\text{USb}_{0.8}\text{Te}_{0.2}$ ", *Phys. Rev.*, B52, 4409-19, (1995).

D.F. Paul, M.J. Cooper, and W.G. Stirling, "Design of an X-ray Beamline on a Bending Magnet at the ESRF For Magnetic and High Resolution Diffraction", *Rev. Sci. Instrum.*, 66/2, 1741-44, (1995).

P. Swaddling, D.F. McMorow, R.A. Cowley, R.C.C. Ward, and M.R. Wells, "Determination of the Interfacial Roughness Exponent in Rare Earth Superlattices", *Phys. Rev. Lett.*, 73, 2232 (1994).

D. Watson, E.M. Forgan, W.G. Stirling, W.J. Nuttall, S.C. Perry, M.M.R. Costa, and D. Fort, "Magnetic X-ray Diffraction From Samarium", *J. Magn. and Magn. Mater.*, 140-144, 743-744 (1995).

X.Z. Wu, B.M. Ocko, H. Tang, E.B. Sirota, S.K. Sinha, and M. Deutsch, "Surface Freezing in Binary Mixtures of Alkanes: New Phases and Phase Transitions", *Phys. Rev. Lett.*, 75, 1332 (1995).

M. Yoon, S.G.J. Mochrie, D.M. Zehner, G.M. Watson, and D. Gibbs, "Periodic Step-Bunching on a Miscut Pt(111) Surface", *Surf. Sci.*, 338, 225, (1995).

Beamline X23A2

M. R. Antonio, J. Malinsky, and L. Soderholm, "Synthesis and Properties of Lanthanide-Exchanged Preyssler's Heteropolyanions", *Materials Research Society Proceedings*, 368, 223, (1995)..

Y. Azuma, H.G. Berry, D.S. Gemmell, J. Suleiman, M. Westerlind, I.A. Sellin, J.C. Woicik, and J.P. Kirkland, "Attenuation of Photons at 3 to 14 keV Energies in Helium", *Phys. Rev.*, A51, 447, (1995).

B.B. Buchanan, J.J. Bucher, D.E. Carlson, N.M. Edelstein, E.A. Hudson, N. Kaltsoyannis, T. Leighton, W. Lukens, H. Nitsche, T. Reich, K. Roberts, D.K. Shuh, P. Torretto, J.C. Woicik, W-S. Yang, A. Yee, and B.C. Yee, "A XANES and EXAFS Investigation of the Speciation of Selenium Following Bacterial Uptake", *Inorg. Chem.*, 34, 1617, (1995).

P. Crespo, A. Hernando, A. Garcia Escorial, K.M. Kemner, and V.G. Harris, "Extended X-ray Absorption Fine Structure Studies of Heat-treated FCC-FeCu Powders Processed via High-Energy Ball-Milling", *J. Appl. Phys.*, 76, 6322, (1994).

M. Fernandez-Garcia, C. Marquez Alvarez, and G.L. Haller, "XANES-TPR Study of Cu-Pd Bimetallic Catalysts: Application of Factor Analysis", *J. of Phys. Chem.*, 99, 12565, (1995).

C.L. Foiles, M.R. Franklin, R. Loloee, R. Clarke, and T.I. Morrison, "EXAFS Study of Co/Cu Multilayers: MBE Versus Sputtered", Application of Synchrotron Radiation Techniques to Materials Science II, edited by L.J. Terminello, N.D. Shinn, G.E. Ice, K.L. D'Amico, and D.L. Perry, Materials Research Society Symposium Proceedings, 375, 207-212, (1995).

K.M. Kemner, B.A. Bunker, H. Luo, N. Samarth, J.K. Furdyna, M.R. Weidmann, and K.E. Newman, "Atomic Rearrangement at Interfaces in ZnTe/CdSe Superlattices", *Phys. Rev.*, B50, 4327, (1994).

K.M. Kemner, A.J. Kropf, and B.A. Bunker, "Gas-amplified Electron-yield X-ray Detection at Low Temperatures", *Rev. Sci. Instrum.*, 65, 3667, (1994).

W. Lin, S. Yitzchaik, W. Lin, A. Malik, M.K. Durbin, A.G. Richter, G.K. Wong, P. Dutta, and T.J. Marks, "New Nonlinear Optical Materials: Expedient Topotactic Self-Assembly of Acentric Chromophoric Superlattices", *Angew. Chem. Int. Ed Engl.*, 34, 1497, (1995).

R.A. Mayanovic, and B.A. Bunker, "Observation of Anisotropic Vibrational Amplitudes due to Thermal Motion at a Cu/Al₂O₃ Interface", *Phys. Lett.*, A202, 225, (1995).

R.A. Mayanovic, Q. Lu, B.A. Bunker, A.J. Kropf, and J.R. Buschert, "Glancing Angle XAFS and X-ray Reflectivity Study of Cu Thermal Vibration Amplitude at the Cu-Al₂O₃ Interface", *Physica B*, 208, 405, (1995).

J. McBreen, X.Q. Yang, H.S. Lee, and Y. Okamoto, "X-ray Absorption Studies of Mixed Salt Polymer Electrolytes: ZnBr₂/CaBr₂-PEO, ZnBr₂/LiBr-PEO, and ZnBr₂/RbBr-PEO Complexes", *J. Electrochem. Soc.*, 142, 348, (1995).

D.A. McKeown, "X-ray Absorption Spectroscopic Study of Cu in an Amorphous Cu-silicate: Chrysocolla", *J. Non-Crystalline Solids*, 180, 1, (1994).

S. Mukerjee, S. Srinivasan, M.P. Soriaga, and J. McBreen, "Effect of Preparation Conditions of Pt Alloys on Their Electronic, Structural, and Electrocatalytic Activities for Oxygen Reduction: XRD, XAS and Electrochemical Studies", *J. Phys. Chem.*, 99, 4577, (1995).

S. Mukerjee, S. Srinivasan, M.P. Soriaga, and J. McBreen, "Role of Structural and Electronic Properties of Pt and Pt Alloys on Electrocatalysis of Oxygen Reduction: An *in situ* XANES and EXAFS Investigation", *J. Electrochem. Soc.*, 142, 1409, (1995).

U. Staub, M.R. Antonio, L. Soderholm, M. Guillaume, W. Henggeler, and A. Furrer, "Tb Oxidation State and Hybridization in Y_{0.9}Tb_{0.9}Ba₂Cu₃O_{7.8}: A Magnetic Susceptibility and X-ray Absorption Study", *Phys. Rev.*, B50, 7085, (1994).

J.E. Tabora, and R.J. Davis, "Structure of Fe, Mn-Promoted Sulfated Zirconia Catalyst by X-ray and IR Absorption Spectroscopies", *J. Chem. Soc. Faraday Trans.*, 91, 1825, (1995).

Beamline X23A3

A.J. Allen, and R.A. Livingston, "Small-Angle Scattering Study of Concrete Microstructure as a Function of Silica Fume, Fly Ash or Other Pozzolonic Additions", Proc. 5Th CANMET/ACI Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Edited by V.M. Malhotra, American Concrete Institute, Detroit, Mi, pp. 1179-1200, (1995).

I. Baker, F. Liu, M. Dudley, and D.R. Black, "In situ Synchrotron Radiation X-ray Topographic Studies of Polycrystalline Ice", Proc. IAHR-94, Trondheim, Norway, pp. 416-425, (1995).

D.R. Black, H.E. Burdette, L. Robins, M.A. Plano, M.D. Moyer, M.A. Moreno, L. Pan, D. Kania, and W. Banholzer, "The Defect Microstructure of Thick Homoepitaxial Diamond Films", Proc. ICNDST-4, Kobe, Japan, pp. 251-256, (1994).

D.R. Black, H. Burdette, R. Linares, and P. Doering, "X-ray Diffraction Imaging of Free-Standing CVD Diamond Films", Proc. 4Th Int'l Symp. On Diamond Materials, Reno, NV, pp. 467-472, (1995).

D. Black, H. Burdette, M.A. Plano, M.D. Moyer, M. Moreno, J. Ager, and A. Chen, "Observation of Individual Defects in a Homoepitaxial Diamond Film", Proc. 4Th Int'l Symp. On Diamond Materials, Reno, NV, p.564, (1995).

L. Cassagrande, D. Larson, D. DiMarzio, J. Wu, M. Dudley, D.R. Black, and H. Burdette, "Growth of Large-Area High-Quality CdZnTe Substrates by Computer-Controlled Vertical Bridgman Method", SPIE, 2228, 21-32, (1994).

X. Hu, K. Jia, I. Baker, and D. Black, "Dislocation Mobility in HCl-Doped Ice", Application of Synchrotron Radiation Techniques to Materials Science, II, edited by L.J. Terminello, N. Shinn, G.E. Ice, K.L. D'Amico, and D.L. Perry, MRS Symp. Proc., 375, pp. 287-292, (1995).

J. Ilavsky, A.J. Allen, G.G. Long, S. Krueger, H. Herman, C.C. Berndt, and A.N. Goland, "Anisotropy of the Surfaces of Pores in Plasma Sprayed Alumina Deposits", Proc. Of the International Thermal Spray Conference (ITSC '95), Kobe, Japan, pp. 483-488, (1995).

S. Krueger, G.J. Olson, D. Johnsonbaugh, and T.J. Beveridge, "Characterization of The Binding of Gallium, Platinum, and Uranium to *Pseudomonas Fluorescens* by Small Angle X-ray Scattering and Transmission Electron Microscopy", Appl. & Environ. Microbiol., 59, 4056-4064, (1993).

W.E. Luecke, S.M. Wiederhorn, B.J. Hockey, R.F. Krause, and G.G. Long, "Cavitation Contributes Substantially to Tensile Creep in Silicon Nitride", J. Am. Ceram. Soc., 78/8, 2085-2096, (1995).

M.A. Plano, M.D. Moyer, M. A. Moreno, D.R. Black, H.E. Burdette, L. Robins, L.S. Pan, D.R. Kania, and W. Banholzer, "Properties of Thick Homoepitaxial Diamond Films", in Diamond, SiC and Nitride wide Bandgap Semiconductors, edited by C. Carter, Jr., G. Gildenblat, S. Nakamura, and R. Nemancih, MRS Proc., 339, pp. 307-312, (1994).

S.M. Wiederhorn, W.E. Luecke, B.J. Hockey, and G.G. Long, "Creep Damage Mechanisms in Si_3N_4 ", in Tailoring of Mechanical Properties of Si_3N_4 Ceramics, edited by M.J. Hoffmann, and G. Petzow, Kluwer Academic Publishers, the Netherlands, pp. 305-326, (1994).

Beamline X23B

G. M. Chow, L. K. Kurihara, K. M. Kemner, P. E. Schoen, W. T. Elam, A. Ervin, S. Keller, Y. D. Zhang, J. Budnick, and T. Ambrose, "Structural, Morphological and Magnetic Study of Nanocrystalline Cobalt-Copper Powders Synthesized by the Polyol Process", J. of Mater. Res., 10, 1546, (1995).

P. Crespo, A. Hernando, A. Garcia Escorial, K. M. Kemner, and V. G. Harris, "Extended X-ray Absorption Fine Structure Studies of Heat-Treated FCC- $\text{Fe}_{50}\text{Cu}_{50}$ Powders Processed via High-Energy Ball-Milling", J. Appl. Phys., 76 /10, 6322-6324, (1994).

K. M. Kemner, W. T. Elam, D. B. Hunter, and P. M. Bertsch, "EXAFS Studies of CsBr-dibenzo-18-crown-6 ether Solutions", Physica B, 208/209, 735, (1995).

K. M. Kemner, V. G. Harris, W. T. Elam, and J. C. Lodder, "EXAFS Studies and Simulations of Local Anisotropy in $\text{Co}_{78}\text{Cr}_{22}$ Films", *Mat. Res. Soc. Symp. Proc.* 375, 21, (1995).

K. M. Kemner, V. G. Harris, W. T. Elam, and J. C. Lodder, "Polarization-Dependent EXAFS Studies of Chemical and Structural Anisotropy in Sputter-deposited $\text{Co}_{78}\text{Cr}_{22}$ Films", *IEEE Trans. Magn.*, 30/6, 4017, (1994).

J.P. Kirkland, and W.T. Elam, "An UHV-Compatible Fixed-exit Two-crystal Monochromator", *Rev. Sci. Instrum.*, 66/2, 2135-2137, (1995).

J.P. Kirkland, and W.T. Elam, "The Naval Research Laboratory's New Hard X-ray Beamline at the National Synchrotron Light Source", *Rev. Sci. Instrum.*, 66 (2), 1709-1711, (1995).

J.P. Kirkland, V.E. Kovantsev, C.M. Dozier, J.V. Gilfrich, W.M. Gibson, Q.-F. Xiao, and K. Umezawa, "Wavelength-dispersive X-ray Fluorescence Detector", *Rev. Sci. Instrum.*, 66/2, 1410-1412, (1995).

K.M. Robinson, and W.E. O'Grady "X-ray Diffraction and Electrochemical Study on the Oxidation of Flame Annealed Au (100) Single Crystal Surfaces", *J. Electroanal. Chem.*, 384, 139-144, (1995).

Beamline X24C

V.M. Bermudez, and J.P. Long, "Characterization of Reconstructed SiC(100) Surfaces Using Soft X-ray Photoemission Spectroscopy", *Appl. Phys. Lett.*, 66, 475, (1995).

B.S. Itchkawitz, J.P. Long, T. Schedl-Niedrig, M.N. Kabler, A.M. Bradshaw, R. Schlögl, and W.R. Hunter, "Photoemission and C 1s Near-edge Absorption From Photopolymerized C_{60} Films", *Chem. Phys. Lett.*, 243, 211, (1995).

T. Kendelewicz, J.E. Klepeis, J.C. Woicik, S.H. Southworth, C. Mailhiet, M. VanSchilfgaarde, M. Methfessel, A. Herrera-Gomez, and K.E. Miyano, "Large-Angle Bond-Rotation Relaxation for CdTe(110)", *Phys. Rev.*, B51, 10774, (1995).

W.R.L. Lambrecht, B. Segall, J. Rife, W.R. Hunter, and D.K. Wickenden, "UV Reflectivity of GaN: Theory and Experiment", *Phys. Rev.*, B51, 13516, (1995).

M.A. MacDonald, S.H. Southworth, J.C. Levin, A. Henins, R.D. Deslattes, T. LeBrun, Y. Azuma, P.L. Cowan, and B.A. Karlin, "Evolution of X-ray Resonance Raman Scattering into X-ray Fluorescence from the Excitation of Xenon Near the L3 Edge", *Phys. Rev.*, A51, 3598, (1995).

J.C. Woicik, J.G. Pelligrino, S.H. Southworth, P.S. Shaw, B.A. Karlin, C.E. Bouldin, and K.E. Miyano, "Accommodation of Strain in Ultra-thin InAs/GaAs Films", *Phys. Rev.*, B52, R2281, (1995)..

Beamline X25

L.E. Berman, "Preserving the High Source Brightness with X-Ray Beam Line Optics", *Rev. Sci. Instrum.*, 66, 2041-2047, (1995).

S. Brauer, G.B. Stephenson, and M. Sutton, "Perfect Crystals in the Asymmetric Bragg Geometry as Optical Elements for Coherent X-Ray Beams", *J. Synch. Rad.*, 2, 163-173, (1995).

J.D. Brock, A.C. Finnefrock, K.L. Ringland, and E. Sweetland, "Detailed Structure of a Charge-Density Wave in a Quenched Random Field", *Phys. Rev. Lett.*, 73, 3588-3591, (1994).

- Y. Cho, S. Gorina, P.D. Jeffrey, and N.P. Pavletich, "Crystal Structure of a p53 Tumor Suppressor-DNA Complex: Understanding Tumorigenic Mutations", *Science*, 265, 346, (1994).
- F.M.F. de Groot, S. Pizzini, A. Fontaine, K. Hämäläinen, C.C. Kao, and J.B. Hastings, "Local-Spin-Selective X-Ray Absorption and X-Ray Magnetic Circular Dichroism of MnP", *Phys. Rev.*, B51, 1045-1052, (1995).
- S.B. Dierker, R. Pindak, R.M. Fleming, I.K. Robinson, and L. Berman, "X-ray Photon Correlation Spectroscopy Study of Brownian Motion of Gold Colloids in Glycerol", *Phys. Rev. Lett.*, 75, 449-452, (1995).
- W. Dmowski, R.J. McQueeney, T. Egami, Y.P. Feng, S.K. Sinha, T. Hinatsu, and S. Uchida, "Temperature Dependent X-Ray Diffuse Scattering from Single Crystals of La-Sr-Cu-O", *Phys. Rev.*, B52, 6829-6839, (1995).
- B.A. Everitt, M.B. Salamon, B.J. Park, C.P. Flynn, T. Thurston, and D. Gibbs, "X-Ray Magnetic Scattering from Nonmagnetic Lu in a DyLu Alloy", *Phys. Rev. Lett.*, 75, 3182-3185, (1995).
- M.M. Grush, G. Christou, K. Hämäläinen, and S.P. Cramer, "Site-Selective XANES and EXAFS: A Demonstration with Manganese Mixtures and Mixed-Valence Complexes", *J. Am. Chem. Soc.*, 117, 5895-5896, (1995).
- C.W. Müller, F.A. Rey, M. Sodeoka, G.L. Verdine, and S.C. Harrison, "Structure of the NF- κ B p50 Homodimer Bound to DNA", *Nature*, 373, 311-317, (1995).
- M.J. Regan, E.H. Kawamoto, S. Lee, P.S. Pershan, N. Maskil, M. Deutsch, O.M. Magnussen, B.M. Ocko, and L.E. Berman, "Surface Layering in Liquid Gallium: X-Ray Reflectivity Study", *Phys. Rev. Lett.*, 75, 2498-2501, (1995).
- J. Sondek, D.G. Lambright, J.P. Noel, H.E. Hamm, and P.B. Sigler, "GTPase Mechanism of Gproteins from the 1.7 Å Crystal Structure of Transducin α -GDP- AlF_4^- ", *Nature*, 372, 276-279, (1994).
- S. Song, and S.G.J. Mochrie, "Attractive Step-Step Interactions, Tricriticality, and Faceting in the Orientational Phase Diagram of Silicon Surfaces Between [113] and [114]", *Phys. Rev.*, B51, 10068-10084, (1995).
- S. Song, S.G.J. Mochrie, and G.B. Stephenson, "Faceting Kinetics of Stepped Si(113) Surfaces: A Time-Resolved X-Ray Scattering Study", *Phys. Rev. Lett.*, 74, 5240-5243, (1995).

Beamline X26A

- A.J. Aldykiewicz, Jr., H.S. Isaacs, and A.J. Davenport, "The Investigation of Cerium as a Cathodic Inhibitor for Aluminum-Copper Alloys", *J. Electrochem. Soc.*, 142, 3342-3350, (1995).
- A.J. Anderson, R.A. Mayanovic, and S. Bajt, "Determination of the Local Structure and Speciation of Zinc Complexes in Individual Fluid Inclusions by Micro-XAFS", *The Canadian Mineral*, 33, 499-508, (1995).
- S. Bajt, and A.L. Hanson, "An Investigation of the Iron Pre-edge XANES Structure", *Rev. Sci. Instrum.*, 66, 1502-1504, (1994).
- S. Bajt, S.R. Sutton, and J.S. Delaney, "Microanalysis of Iron Oxidation States in Earth and Planetary Materials", *Physica*, B208/209, 243-244, (1995).
- S. Bajt, S.R. Sutton, and J.S. Delaney, "Microanalysis of Iron Oxidation States in Silicates and Oxides Using X-ray Absorption Near Edge Structure (XANES)", *Geochim. Cosmochim. Acta*, 58, 5209-5218, (1995).

C. Dalpe, D.R. Baker, and S.R. Sutton, "Synchrotron X-ray-Fluorescence and Laser-Ablation ICP-MS Microprobes: Useful Instruments for Analysis of Experimental Run-Products", *The Canadian Mineral*, 33, 481-498, (1995).

A.J. Davenport, and M. Sansone, "High Resolution *in situ* XANES Investigation of the Nature of the Passive Film on Iron in pH 8.4 Borate Buffer", *J. Electrochem. Soc.*, 142, 725-730, (1995).

A.J. Davenport, J.A. Bardwell, and C.M. Vitus, "*In situ* XANES Study of Galvanostatic Reduction of the Passive Film on Iron", *J. Electrochem. Soc.*, 142, 721-724, (1995).

H. Isaacs, J.-H. Cho, M.L. Rivers, and S.R. Sutton, "*In situ* X-ray Microprobe Study of Salt Layer During Anodic Dissolution of Stainless Steel in Chloride Solution", *J. Electrochemical Soc.*, 142/4, 1111-1118, (1995).

A. Lanzirotti and G.N. Hanson, "U-Pb Dating of Major and Accessory Minerals Formed During Metamorphism and Deformation of Metapelites", *Geochimica et Cosmochimica Acta*, 59, 2513-2526, (1995).

R.A. Mayanovic, A.J. Anderson, and S. Bajt, "Development of Micro-XAFS: Applications to Studies of Single Fluid Inclusions", *Physica*, B208/209, 239-240, (1995).

P. Northup, and R.J. Reeder, "Evidence for The Importance of Growth-Surface Structure to Trace Element Incorporation in Topaz", *American Mineralogist*, 79, 1167-1175, (1994).

J. Rakovan and R.J. Reeder, "Differential Incorporation of Trace Elements and Dissymmetrization in Apatite: The role of Surface Structure During growth", *American Mineralogist*, 79, 892-903, (1994).

S. Shah, A. Ward, and A.J. Davenport, "Characterization of Tellerium-Based Conversion Coatings with XANES and FTIR", *Corrosion*, 51, 67-70, (1995).

S. Sutton, S. Bajt, J. Delaney, D. Schulze, and T. Tokunaga, "Synchrotron X-ray Fluorescence Microprobe: Quantification and Mapping of Mixed Valence State Samples Using Micro-XANES", *Rev. Sci. Instrum.*, 66, 1464-1467, (1995).

K.L. Thomas, et al., "An Asteroidal Breccia: The Anatomy of a Cluster IDP", *Geochimica et Cosmochimica Acta*, 59/13, 2797-2815, (1995).

T. Tokunaga, S.R. Sutton, and S. Bajt, "Mapping of Selenium Concentrations in Soil Aggregates with Synchrotron X-ray Fluorescence Microprobe", *Soil Science*, 158, 421-433, (1994).

Beamline X26C

P.-C. Wang, C.S. Cargill III, and I.C. Noyan, "Strain Measurements and Laue Diffraction With Microbeams", *MRS Symp. Proc.*, 375, 247, (1995).

B.X. Yang, M.L. Rivers, W. Schildkamp and P. Eng, "GeoCARS Micro-Focusing Kirkpatrick-Baez Mirror Bender Development", *Rev. Sci. Instrum.*, 66, 2278-2280, (1995).

PUBLICATIONS

NSLS STAFF

J.L. Bantignies, C. Moulin, H. Dexpert, A.M. Flank, And G.P. Williams, "Asphaltene Adsorption on Kaolinite: Characterization by Infrared Microspectroscopy and X-ray Adsorption Spectroscopy", *Compte Rendu del'Acad. Sci. Paris*, 320, 699, (1995), BNL 61879.

K. Batchelor, M. Babzien, I. Ben-Zvi, R. Fernow, J. Fischer, A. Fisher, R. Malone, I. Pogorelsky, T. Srinivasan-Rao, J. Sheehan, and X. Wang, "Operational Experience on the Brookhaven National Laboratory Accelerator Test Facility", Proceedings 4th European Particle Accelerator Conference, edited by V. Suller and C. Pette-Jean-Genex, World Scientific, Vol. 1, pp. 736-738, (1994), BNL 60739.

I. Ben-Zvi, "Milestone Experiments for Single Pass UV/X-Ray FELs", *Nucl. Instrum. And Meths. In Phys. Res.*, A358, 54, (1995). BNL 60827.

U. Bergmann, S.D. Shastri, D.P. Siddons, B.W. Batterman, and J.D. Hastings, "Temperature Dependence of Nuclear Forward Scattering of Synchrotron Radiation of α - ^{57}Fe ", *Phys. Rev.*, B50/9, 5957-5961, (1994), BNL 60854.

L.E. Berman, "Preserving the High Source Brightness with X-ray Beamline Optics", *Rev. Sci. Instrum.*, 66, 2041-2047, (1995), BNL 60859.

L.E. Berman, "Structural Biology at the National Synchrotron Light Source", *Synch. Rad. News*, 8/4, 11-15, (1995), BNL 62171.

L.E. Berman, "Review of Optical Engineering Volume 34, Special Edition on High Heat Flux Optical Engineering", *Synch. Rad. News*, 8/4, 37, (1995), BNL 62176.

R. Biscardi, G. Ramirez, and G.P. Williams, "Effects of RF Side-Bands on Spectral Reproducibility for Infrared Synchrotron Radiation", *Rev. Sci. Instrum.*, 66, 1856, (1995), BNL 60862.

E.B. Blum, and L. Solomon, "Calculated and Measured Fields in Superferric Wiggler Magnets", The Art and Science of Magnet Design, A Festschrift in Honor of Klaus Halbach, Lawrence Berkeley Laboratory, Vol. 1, pp. 29-37, (1995), BNL 60980.

E. Bozoki, "Closed Orbit Related Problems: Correction, Feedback and Analysis", AIP Conference Proceedings, 315, p. 43, 1994, BNL 61251.

E. Bozoki, and A. Friedman, "The Use of Neural Networks in the Orbit Control of Accelerators and Storage Rings", AIP Conference Proceedings, 315, p. 103, 1994, BNL 61253.

E. Bozoki, and A. Friedman, "Neural Networks and Orbit Control in Accelerators", Proceedings 4th European Particle Accelerator Conference, London, 2, p. 1589, (1994), BNL 60586.

K. Breuer, K.E. Smith, D. Goldberg, M. Greenblatt, W. McCarroll, and S.L. Hulbert, "Defects in Quasi-One Dimensional Oxide Conductors: $K_{0.3}MoO_3$ ", Mat. Res. Soc. Symp. Proc., 375, 133, (1995), BNL 61406.

G.L. Carr, M. Hanfland, and G.P. Williams, "The Mid-Infrared Beamline at the NSLS Port U2B", *Rev. Sci. Instrum.*, 66, 1643, (1995), BNL 60893.

D. Chapman, W. Thomlinson, N.F. Gmur, J.P. Dervan, T. Stavola, J. Giacomini, H. Gordon, E. Rubenstein, W. Lavender, C. Schulze, and A.C. Thompson, "Effects of Spatial Resolution and Spectral Purity on Transvenous Coronary Angiography Images", *Rev. Sci. Instrum.*, 66/2, 13291331, (1995), BNL 60861.

C.L. Foerster, "Ultra-High Vacuum System of the Brookhaven National Synchrotron Light Source", Proceedings International Conference on Vacuum Science & Technology and SRS Vacuum Systems- INCOVAST 95, Indore, India, Vol. 1, pp. 36-57, (1995), BNL 62537.

C.L. Foerster, C. Lanni, C. Perkins, M. Calderon, and W. Barletta, "Photon Stimulated Desorption (PSD) Measurements of Extruded Copper and of Welded Copper Beam Chambers for the PEP II Asymmetric B-factory", *J. Vac. Sci. Technol.*, A13/3, 581, (1995), BNL 61082.

Fontana, J.R., Kimura, W.D., Steinhauer, L.C., Pogorelsky, I., "Design Analysis for a 100 MeV Inverse Cerenkov Laser Accelerator", Proceedings of the 1993 Particle Accelerator Conference, Washington, DC, p. 2614, (1993), BNL 60092, February 1994.

A. Friedman, and E. Bozoki, "A Digital Feedback System for Transverse Orbit Stabilization in the NSLS Rings", Proceedings International Conference on Accelerator and Large Experimental Physics Control Systems, Berlin, Germany, NIM, A352, p. 393, 1995, BNL 49670.

A. Friedman, and E. Bozoki, "A Digital Feedback System for Transverse Orbit Stabilization", Proceedings 4th European Particle Accelerator Conference, London, England, 2, p.1586, 1994, BNL 60629.

A. Friedman, and E. Bozoki, "Eigenvector Method for Optimized Orbit Correction", AIP Conference Proceedings, 315, p. 43, 1994, BNL 61252.

L.R. Furenlid, M.W. Renner, and E. Fujita, "XAS Studies of Ni(I), Ni(II), and Ni(III) Complexes", *Physica*, B208/209, 739-742, (1994), BNL 61084.

N.F. Gmur, D. Chapman, W. Thomlinson, A.C. Thompson, W.M. Lavender, K. Scalia, N. Malloy, J. Mangano, and J. Jacob, "NSLS Transvenous Coronary Angiography Beamline Upgrade and Advanced Technology Initiatives", *Rev. Sci. Instrum.*, 66/2, 1357-1360, (1995), BNL 60857.

C.J. Hirschmugl, and G.P. Williams, "Chemical Shifts and Coupling Interactions for the Bonding Vibrational Modes for CO/Cu(111) and (100) Surfaces", *Phys. Rev.*, B52, 14177, (1995), BNL 62539.

C.J. Hirschmugl, and G.P. Williams, "Signal to Noise Improvements with a New Far-IR RapidScan Michelson Interferometer", *Rev. Sci. Instrum.*, 66, 1487, (1995), BNL 60892.

C.J. Hirschmugl, and G.P. Williams, "Infrared Synchrotron Radiation Introduction and History", *Synch. Rad. News*, 8/5, 8, (1995), BNL 62171.

E.D. Johnson, "Scientific Opportunities for FEL Amplifier based VUV and X-Ray Research", *Nucl. Instrum. and Meths. in Phys. Res.*, A358, 544-547, (1995), BNL 61411.

E.D. Johnson, D.P. Siddons, J.Z. Larese, and J.B. Hastings, "Observation of Nuclear Forward Scattering from ^{83}Kr in Bulk and Monolayer Films", *Phys. Rev.*, B15/12, 7909-7911, (1995), BNL 61404.

C.C. Kao, K. Hamalainen, M. Krisch, D.P. Siddons, T. Oversluizen, and J.B. Hastings, "Optical Design and Performance of the Inelastic Scattering Beamline at the National Synchrotron Light Source", *Rev. Sci. Instrum.*, 66, 1699, (1995), BNL 61410.

W.D. Kimura, G.H. Kim, R.D. Romea, L.C. Steinhauer, I. Pogorelsky, K.P. Kusche, R.C. Fernow, X. Wang, and Y. Liu, "Laser Acceleration of Relativistic Electrons Using the Inverse Cerenkov Effect", *Phys. Rev. Letts.*, 74/4, 546-549, (1995), BNL 60522.

S. Krinsky, "Optimization of Accelerator System Performance at the NSLS", *Rev. Sci. Instrum.*, 66, 2017, (1995). BNL 60766.

B. LaFontaine, A.A. MacDowell, Z. Tan, D.L. White, G.N. Taylor, O.R. Wood, J.E. Bjorkholm, D.M. Tennant, and S. Hulbert, "Submicron, Soft X-Ray Fluorescence Imaging", *Appl. Phys. Letts.*, 66, 282-284, (1995), BNL 61698.

C.L.A. Lamont, B.N.J. Persson, and G.P. Williams, "Dynamics of Atomic Adsorbates: Hydrogen on Cu(111)", *Chem. Phys. Letts.*, 243, 249, (1995), BNL 62538.

Y. Liu, Y. Gagnon, J. Gauthier, L. Furenid, P. L'Heureux, M. Auger, O. Nureki, S. Yokoyama, and J. Lapointe, "The Zinc Binding Site of Escherichia coli Glutamyl-tRNA Synthetase is Located in the Acceptor-Binding Domain", *J. Of Biol. Chem.*, 270, 15162-15169, (1995). BNL 61412.

J. Milne, E.D. Johnson, and G.C. Smith, "Use of Primary Electron Counting for Detection of Ultra-Soft X-rays with a Low-Pressure Multi-Step Gaseous Detector", *Rev. Sci. Instrum.*, 66/2, 2330-2332, (1995), BNL 61413.

I. Pogorelsky, J. Fischer, K.P. Kusche, M. Babzien, N.A. Kurnit, I.J. Bigio, R.F. Harrison, and T. Shimada, "Subnanosecond Multi-Gigawatt CO₂ Laser", *IEEE Journal of Quantum Electronics*, 31, p. 556, (1995), BNL 60399.

I. Pogorelsky, W.D. Kimura, C.H. Fisher, F. Kannari, and N.A. Kurnit, "Approach to Compact Terawatt CO₂ Laser System for Particle Acceleration", *6th Workshop on Advanced Accelerator Concepts*, Lake Geneva, Wisconsin, 335, p. 405, (1995), BNL 60826.

I. Pogorelsky, W.D. Kimura, and Y. Liu, "Waveguiding by Axicon-Focused Laser Beams", *6th Workshop on Advanced Accelerator Concepts*, Lake Geneva, Wisconsin, AIP, 335, p. 419, (1995), BNL 60774.

X.Z. Qui, X.J. Wang, K. Batchelor, and I. Ben-Zvi, "Conceptual Design of a Charged Particle Beam Energy Spectrometer Utilizing Transition Radiation Grating", *Nucl. Inst. And Meth. In Phys. Res.*, A363, 520-525, (1995), BNL 61849.

J.A. Reffner, P.A. Martoglio, and G.P. Williams, "FT-IR Microscopical Analysis with Synchrotron Radiation: The Microscope Optics and System Performance", *Rev. Sci. Instrum.*, 66, 1298, (1995), BNL 61083.

- C. Schulze, and D. Chapman, "PEPO: A Program for the Calculation of the Reflectivity of Cylindrically Bent Laue Crystal Monochromators", *Rev. Sci. Instrum.*, **66/2**, 2220-2223, (1995), BNL 61689.
- D.P. Siddons, J.B. Hastings, U. Bergmann, F. Sette, and M. Krisch, "Mossbauer Spectroscopy using Synchrotron Radiation: Overcoming Detector Limitations", *Nucl. Instrum. and Meth. in Phys. Res.*, **B103**, 371-375, (1995), BNL 61407.
- B. Sinkovic, E. Shekel, and S.L. Hulbert, "Spin-Resolved Fe $L_3M_{45}M_{45}$ Auger Transition on and Off-Resonance-The Effect of Exchange-Correlation", *Phys. Rev.*, **B52**, 15703, (1995), BNL 62536.
- B. Sinkovic, E. Shekel, and S.L. Hulbert, "Spin-Resolved Iron Surface Density of States", *Phys. Rev.*, **B52**, R8696, (1995), BNL 61405.
- L. Solomon, W. Graves, and I. Lehrman, "Magnetic Field Measurements of the Harmonic Generation FEL Superconducting Undulator at BNL-NSLS", *Nucl. Instrum. And Meths.*, **358**, 411-413, (1995), BNL 61409.
- P.M. Stefan, S. Krinsky, G. Rakowsky, and L. Solomon, "Operation of a Small-Gap Undulator on the NSLS X-ray Ring", Art and Science of Magnet Design, A Festschrift in Honor of Klaus Halbach, p. 161, (1995), BNL 61053.
- X.J. Wang, T. Srinivasan-Rao, K. Batchelor, I. Ben-Zvi, and J. Fischer, "Measurements on Photoelectrons from a Magnesium Cathode in a Microwave Electron Gun", *Nucl. Instrum. And Meths. In Phys. Res.*, **A356**, 159-166, (1995), BNL 60356.
- X.J. Wang, I. Pogorelsky, K. Kutsche, Y. Liu, and R. Fernow, "Inverse Cerenkov Laser Acceleration Experiment at the ATF", Proceedings of the 17th International Linac Conference, pp. 810-812, (1994), BNL 60737.
- X.J. Wang, T. Srinivasan-Rao, K. Batchelor, I. Ben-Zvi, and J. Fischer, "Photoelectrons Beam Measurement from a Magnesium Cathode in a RF Electron Gun", Proceedings of 17th International Linac Conference, pp. 407-409, (1994), BNL 60738.
- G.P. Williams, J. Reffner, and P. Martoglio, "FT-IR Microscopical Analysis with Synchrotron Radiation: The Microscope and System Performance", *Rev. Sci. Instrum.*, **66**, 1298, (1995), BNL 61083.
- X.Y. Wu, F.A. Dilmanian, Z. Chen, B. Ren, D.N. Slatkin, D. Chapman, M. Shleifer, F.A. Staicu, and W. Thomlinson, "Multiple Energy Computed Tomography (MECT) at the NSLS: Status Report", *Rev. Sci. Instrum.*, **66/2**, 1346-1347, (1995), BNL
- L.H. Yu, "Exponential Decay of Wavelength in a Dissipative System", *Phys. Letts.*, **A202**, 167, (1995), BNL 60927.
- L.H. Yu, C.M. Hung, D. Li, and S. Krinsky, "Scaling Function for Free-Electron-Laser Gain Including Alternating Gradient Focusing", *Phys. Rev. Lett.*, **E51**, 813, (1995), BNL 49122.
- J. Zegenhagen, T. Siegrist, E. Fontes, L.E. Berman, and J.R. Patel, "Epitaxy of Ultrathin Films of $Yb_2Cu_3O_{7-\delta}$ on $SrTiO_3(001)$ Investigate With X-ray Standing Waves", *Solid State Commun.*, **93**, 763, (1995), BNL 60863.

REPORTS

BNL FORMAL AND INFORMAL REPORTS

N. Gmur, "Research by Industry at the National Synchrotron Light Source", BNL 61553, March 1995.

Y. Liu, and I.V. Pogorelsky, "Gas Breakdown Limits for Inverse Cherenkov Laser Accelerators", BNL 61876, June 1995.

I.V. Pogorelsky, "ATF CO₂ Laser System Upgrade to Terawatt Peak Power", BNL 61849, 1995.

I.V. Pogorelsky, "Electron Acceleration in Plasma Channels with Terawatt CO₂ Laser", BNL 61482, February 1995.

I.V. Pogorelsky, "High-Intensity Laser Synchrotron X-ray Source", BNL 62447, 1995.

X.Z. Qiu, X.J. Wang, and I. Ben-Zvi, "Proposal for Using Optical Transition Radiation for Electron Beam Alignment and Emittance Measurement for the Free Electron Laser Experiments at ATF", BNL 60999, November 1994.

E.Z. Rothman, "1994 Activity Report, National Synchrotron Light Source" BNL 52455, March 1995.

J. Safranek, and S. Krinsky, "Coupling Correction Using Closed Orbit Measurements", BNL 61246, December 1994.

J. Safranek, and M. Lee, "Calibration of the X-ray Ring Quadrupoles, BPMs and Orbit Correctors using the Measured Orbit Response Matrix", BNL 61250, December 1994.

X.J. Wang, K. Batchelor, I. Ben-Zvi, and M. Woodle, "Proposal for Testing a New Generation Photocathode RF Gun at Accelerator Test Facility", BNL 60979, October 1994.