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NATIONAL SYNCHROTRON LIGHT SOURCE

(For the period October 1, 1992 through September 30, 1993)

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INTRODUCTION

Denis McWhan
NSLS Chairman

The NSLS continues to improve operations and to provide critical R&D needed to enhance the production and utilization of synchrotron radiation. The facility delivered 5847 and 5044 hours of user beam with only 3.1% and 6.4% unscheduled downtime on the VUV and X-Ray Rings respectively. These are unprecedented numbers, and the staff is to be commended for its efforts in increasing both the reliability and stability of the beams.

The figure at right shows the steady increase in amp hours and decrease in unscheduled downtime for the last five years. FY93 was also a banner year for the users. The number of users fluctuates with the coming and going of the more than 900 hundred students and the total number of users who had active guest appointments some time during the year was 3274 of which 480 were from industry. More than 1100 experiments were performed and 649

NSLS Management Group:

(front, from left)
Bill Thomlinson, Associate Chairman;
Denis McWhan, Chairman;
Sam Krinsky, Deputy Chairman.

(back, from left)
Marty Woodle, Mechanical Engineering;
Jerry Hastings, Beamline Support/R & D
Ilan Ben-Zvi, Accelerator Test Facility;
Bill Foyt, Assistant to the Chairman;
John Keane, Electrical Systems;
Richard Heese, Operations.

papers based in part on work done at the NSLS were published. The NSLS is clearly fulfilling its mission as a user facility serving university, industry, and government scientists.

A series of milestones was reached in the operations of the rings. ♦ In July there was a real feeling of satisfaction associated with sending the old Data General computers off to the junkyard now that the new control system based on HP workstations is operating smoothly. ♦ The X-Ray Ring reached an operating current of 500 mA after the 4th RF cavity was installed to provide enough RF power (400 KW). ♦ We are presently running at 2.584 GeV and 438 mA during studies and some template shifts so that users can determine the heating effects of the higher current on the existing beamline optics. ♦ A task force headed by Lonny Berman (NSLS) is trying to establish the safe working current for the insertion device output chambers. It is hoped that routine high current operations with the

insertions device gaps closed can commence in the spring. Coupled with the increase in current, ♦ James Safranek (NSLS) has succeeded in lowering the vertical emittance from 1.0 to 0.2 nanometer radians, and this means that the brightness of the beam can be increased by a factor of ten. The expected brightness on the X1 soft x-ray undulator approaches 10^{18} photons/sec./0.1%b.w./mm²/mrad². With this brightness, ♦ the x-ray microscopy and soft x-ray spectroscopy programs which share the radiation on the X1 undulator will remain competitive for the foreseeable future. ♦ On the VUV Ring, the lifetime has been increased further by powering the fourth harmonic RF cavity. This has been coupled with continued improvements in beam stability. ♦ Planned upgrades of several VUV beamlines have led to the nucleation of new PRT groups interested in the biological, chemical and materials sciences involving industry, university and government laboratory scientists.

NSLS X-RAY AND VUV RING PERFORMANCE

New experimental capabilities continue to flow from the more than 80 beamlines at the NSLS. In FY92 the extensive high heat load optics program on the X25 wiggler beamline, under the direction of Lonny Berman, led to the first demonstration of the use of isotopically enriched synthetic diamond crystals as a prime candidate for monochromators on 3rd generation x-ray sources. This program continues to refine the mounting and cooling

techniques needed for reliable, high resolution scattering studies under high heat load conditions. After extensive studies on the optics needed for inelastic x-ray scattering by Chi-Chang Kao (NSLS) and his colleagues, the X21 wiggler beamline has an active program. Harold Ade (University of North Carolina) continues to extend the frontiers of chemical contrast x-ray microscopy on X1 with his studies on polymer blends. The recent studies done in collaboration with B. Hsiao (DuPont) using x-ray dichroism to determine the orientation of functional groups in the different polymers makes this technique even more powerful. Building on successful programs at

the NSLS in x-ray lithography by IBM and AT&T, Erik Johnson and Peter Siddons have been collaborating with Henry Guckel from the University of Wisconsin on deep x-ray lithography. They have taken the field of micromachining from essentially two dimensional ob-

jects to fully three dimensional objects which range from several millimeters to several tens of millimeters in thickness. Gwyn Williams has initiated a pro-

gram in infrared microscopy on the VUV Ring. The brightness of the VUV Ring has enabled scientists from Spectra-Tech, Inc., Grumann Corporation Research Center, and the Carnegie Geophysical Institute to increase the resolution of IR microscopy from 100 μ to less than 10 μ .

Finally, contracts for the construction of new user set-up space both from X1 to X4 and the structural biology addition from X6 to X12 have been awarded. We look forward to a fall of 1994 completion. At that time each PRT/IDT should have set-up space on the experimental floor.

***The facility provided
5847 and 5044 hours of user beam
with only 3.1% and 6.4% unscheduled downtime
on the VUV and X-Ray Rings
respectively.***

USERS' EXECUTIVE COMMITTEE

Johnny Kirkland

Naval Research Laboratory/SFA Inc.

UEC Chairman

The mission of the Users' Executive Committee (UEC) is to promote and encourage research at the NSLS by communicating the user community needs to the NSLS Department and BNL management. Three Town Meetings were hosted by the UEC during the year to encourage open and informal discussion with the NSLS staff. Following each Town Meeting, the UEC met with NSLS and BNL representatives to jointly address current

user issues. My thanks to the members of the committee and other individuals who have helped by volunteering their time throughout the year to try to make the NSLS a "user-friendly" place.

The NSLS Annual Meeting is the most visible function of the UEC and NSLS Department. Articles on the 1993 meeting and workshops appear later in this Annual Report. The planning committee kept last year's

Users' Executive Committee

(back, from left)

Syed Qadri (NRL) , David Heskett (Univ. of Rhode Island), Paul Lyman (Northwestern Univ.), Carol Hirschmugl (NSLS/Yale), Robert Sweet (BNL Biology), Jon Levin (NIST), Randy Aikire (ANL), Geraldine Lamble (NSLS/NCSU), Jim Long (NRL), and Alastair MacDowell (AT&T).

(front, from left)

Saša Bajt (Univ. of Chicago), Michael Dudley (SUNY at Stony Brook), Jean Jordan-Sweet (IBM), Johnny Kirkland (NRL/SFA), Eva Rothman (NSLS), Ott Kistner (BNL Physics; stand-in for Craig Thorn)

changes: the streamlined pre-registration publicity flyer, the revised registration booklet, the discounted pre-registration fee, complimentary attendance gift, the lunch time special interest group meetings, and the off-site banquet. We added a non-political keynote speaker, a budget for each of the workshop coordinators, and a jobs board operated by the Graduate Student/Post-Doc SPIG. I am pleased to report that because of good attendance, twenty-two Corporate Sponsors, and cost saving measures, the 1993 Annual Meeting produced a budget surplus which will fund user community functions and perhaps some amenities for our users. My thanks to Linda Feierabend, Jean Jordan-Sweet, Randy Alkire, Dave Heskett, Paul Zschack, Susan White-DePace and Eileen Pinkston for all of their effort in putting together a successful User Meeting.

One touching event at the Annual Meeting Banquet was the presentation of a special gift from the UEC to Susan White-DePace, who was stepping down from her

The UEC continues to push for other improvements in services and "quality of life" issues.

job as User Administrator. The UEC wanted to acknowledge all of the work she has done to improve access to the NSLS for the users. She has instituted many of the key features of the User Administration Office and suggested dozens of improvements for the General User program. She has consistently looked out for the best interests of the users, and the UEC wanted to show its appreciation. At the fall Town Meeting and UEC Meeting we were introduced to the new User Administrator, Eva Rothman. The UEC looks forward to working together with the User Administration Office to keep the NSLS a good place for users to do business.

The UEC established two committees this year to provide guidance to the NSLS Administration regarding future operating conditions for the X-Ray Ring and prioritization of VUV Ring upgrades. The X-Ray Ring Operations Committee, headed by Lars Furenlid (NSLS), presented to the PRT spokespersons, the UEC, and the users the options and the ramifications of increased ring energy, reduced source size, and increased ring current operations. The VUV Ring Operations Committee, headed by Paul Lyman (Northwestern University), polled the PRT spokespersons for their preferences to what

**Johnny Kirkland, UEC Chairman
Naval Research Laboratory/ SFA Inc**

improvements were needed most for the VUV Ring, given the NSLS's financial and man-power constraints.

Over the years, many aspects of the NSLS/User interface and "quality of life" have been improved due to the efforts of the Scientific Program Support Committee (SPSC). This year the co-chairpersons are Gwyn Williams (NSLS) and Mike Sagurton (SFA, Inc.). One focus of this year's SPSC has been the end-of-run form submitted by General Users to the User Administration Office after completion of their experiment. If users have had problems that hampered the success of their experiment, then this form should be useful to the NSLS in identifying the source of the problems and making adjustments to prevent them in the future. Unfortunately, a very small percentage of forms were being returned. The SPSC worked on rewording the forms to help identify problems and tried to change the system to improve the number of responses. There was an underlying feeling that all of the needs of the users weren't being met, and the form would help identify those needs to the NSLS Administration. Rather than wait for the results of the new forms to trickle down over the next year or two, Denis McWhan and Jerry Hastings have taken a proactive step to identify and solve problems as they happen. An NSLS scientific staff person will be assigned to meet with each new General User group as they get started with their experiments to make sure that they have all the help they need, and if necessary, identify resources within NSLS and BNL that can help them solve any problems they may encounter.

The UEC continues to push for other improvements in services and "quality of life" issues. We are trying to make sure space is available for an additional lounge in the new expansion of the experimental floor. We are still pushing the NSLS Administration to take measures to reduce noise on the VUV and X-Ray experimental floors. The UEC is pleased to see that many of the recommendations made to Staff Services to improve housing reservations and payments have been made. The reservation system is now computerized and payments for housing can be made with most major credit cards. Although on-site housing has not been increased, renovations are underway to improve exteriors and interiors to make the available housing more comfortable.

UEC sponsorship of the Friday evening graduate student/post-doc get-togethers continues, and we would especially like to recognize the Student SPIG and Carol

Hirschmugl for their efforts in organizing these events.

Finally, 1993 was the year when each beamline was required to implement the Beam Line Operations and Safety Awareness Program (BLOSA). Last year the UEC worked with Associate Chairman Bill Thomlinson to devise a system that was the least painful for beamlines to carry out but met all of the goals of the program. The program for all beamlines began November 1, 1993. Now all new users at each beamline must undergo a prescribed course of instruction and sign a sheet saying that they understood what they were told. The system should insure that each user that shows up to do experiments at the NSLS is aware of the facility and beamline safety systems and resources available within the NSLS. By being aware they should be able to get assistance quickly if they have problems, and in general run their experiments more safely and efficiently.

Scientific Program Support Committee

(left to right): René Holaday (MIT); Brian DeVries (EXXON); Gwyn Williams (NSLS); Malcolm Capel (BNL Biology); Mike Sagurton (SFA, Inc.); missing from photo: Lars Furenlid (NSLS)

ENVIRONMENT, SAFETY AND HEALTH UPDATE

William Thomlinson

Associate Chairman

NSLS

The NSLS continued its efforts in 1993 to balance the priorities of operations for scientific research and the DOE/BNL requirements for a strong Environment, Safety and Health (ES&H) program. The most significant step taken was to formally delegate the responsibilities for ES&H to the Associate Chairman. The intent of this reorganization was to place all ES&H activities in a direct administrative line to the Chairman. By taking this action we are able to coordinate the NSLS response to daily

operation needs, mandated DOE and BNL programs, and emergency situations. In fact, by making these changes the NSLS has been responsive to one of its critical findings in last year's NSLS ES&H Self-Assessment. We are working on improving communication among the ES&H personnel and between our safety staff and the general NSLS user and staff community. Although there are still some weaknesses in the area of communication, we are addressing them.

NSLS Operations Staff:

(back, from left to right) George Jahnes, Gary Weiner, Tony Rodriguez, Pete Ratzke, John Klug
(front, from left to right) Lenny Pharr, Ed Zeitler, Billy Jew, John Aloï, Mike Santana, Steve Kemp, Randy Church,
Charles Bellizzi, missing from photo: Mike Buckley

The NSLS has completed its 1993 NSLS ES&H Self-Assessment. We have improved a lot relative to the 1992 findings in the area of management. Another area of significant progress has been in ES&H training. Under the direction of Denny Klein, the NSLS is compliant with the requirements for radiation safety training, electrical safety training, general employee safety training, etc. The NSLS has established criteria for developing training modules for "on the job" training. One example is our electrical safety training program which may become a model for BNL.

Along these same lines, the Beam Line Operations and Safety Awareness training program (known as BLOSA) has been introduced. Though starting slowly, it has now become an effective tool for the beamline personnel to assure that their users are familiar with the safety and operations of the beamlines. It also provides a good record of beamline utilization. A few wrinkles remain, but we are pleased with the acceptance of this critical safety training interface by the users and beamline staff. The early success is due to the hard work of Nancy Lazarz, Denny Klein, John Klug, Nancye Wright, and several key local contact persons who have provided us with a lot of feedback. The Operations Coordinators are a key element of this program and are working with the User Administrator and the Training Coordinator to insure continued progress and success.

There has been a major effort underway for the past year to reduce the radiation levels on the second floor of the NSLS building. The problem is a very difficult one since the sources have to be identified (booster, VUV Ring, X-Ray Ring), the conditions during which the radiation occurs have to be clarified (injection, normal operations) and then shielding must be designed to effectively eliminate the sources of both gamma radiation and neutrons. Principal staff involved in this program are Andrew Ackerman, Ken Batchelor, Rudy Zantopp, Chris Weilandics, Norman Fewell and the ALARA committee chaired by Peter Stefan. A lot of new shielding has been added to the Booster Ring during the December 1993 shutdown which should really help. Measurements done since the January startup indicate that we may soon be able to eliminate the need to have the office areas posted as controlled areas.

During the past year, very few new ES&H regulations and mandates were imposed on the NSLS. The breathing space has allowed us to implement the programs discussed above and to complete the process of coming into compliance with existing orders. Ken Batchelor brought the NSLS SEAPPM (Safety and Environmental Administrative Policy and Procedures Manual) up to date and Norman Fewell finished the formalization of the NSLS Maintenance Management Program. Looking to the future, we will be increasing communication with users and staff through an ES&H newsletter and plans are being formulated to revise the NSLS user training video. These efforts are intended to preserve the efficient manner in which our training is done and to insure that it is compliant with all DOE regulations. Maintaining our historically safe working environment is obviously a very high priority at the NSLS.

John Klug, Operations Coordinator, setting up the yellow safety board at beamline X21.

USER ADMINISTRATION REPORT

Eva Z. Rothman
User Administration
NSLS

At the end of July, I picked up where Susan White-DePace left off as NSLS User Administrator. Susan has always been an advocate of the user community and won the respect of both users and management, within BNL and outside. Under her guidance, the User Administra-

tion Office has grown from a small operation to a crucial part of the organization. My thanks to the User Administration staff, particularly Eileen Pinkston, for taking on the extra workload during the transitional period and for helping me get oriented quickly.

User Administration Office: (from left to right) Eva Rothman, Eileen Pinkston, Linda Feierabend

NSLS Users in FY93

Figure 1 (left): Number of active users registered in the NSLS database for each year.

Figure 2 (right): Active users by home institution.

Once again the demand for NSLS beam time exceeds the supply, despite the reliable delivery, short injections, and low number of unscheduled down times shown in the ring managers' reports. For this year's three beam cycles, the User Administration Office received a total of 195 new General User proposals, up from 173 last year. In addition, 225 requests for beam time against existing General User proposals were received. Of the 420 requests and proposals, 72% were allocated beam time in FY93. The above numbers represent only a small part of the work being done at the NSLS, since only about 25% of each beamline's operational time is devoted to the General User Program.

Another measure of a facility's scientific contribution is the number of publications printed as a result of research conducted there in whole or in part. In this area as well the NSLS continues its healthy level. The number of publications accepted or in print for FY93, not including abstracts, was 649, compared to 657 last year and 451 the year before.

Refinements and improvements to the NSLS Database continued this year. The NSLS Database allows the User Administration Office to collect statistics about the users and their work based on the information they enter upon registering. It was first brought on line in December of 1991 and since then has been enhanced with additional fields and features such as film badge issuing, training dates, and various reports. Through the efforts of Liz Hicks and Linda Feierabend the database has become an indispensable tool for keeping track of our users.

And keeping track of the users is an ever-increasing task as the NSLS is seeing a rising number of active users (Figure 1). An all-time high of 3274 was reached in FY93. Over 39% of the users registered in the database under the scientific discipline of Nuclear/Optical/General Physics, and over 80 percent of these were involved in the solid state area. Over 60% of all users in FY93 came from universities while about 15% came from private industry. US laboratories, government agencies and other types of institutions supplied the remainder (Figure 2). Although 85% of all users came from US institutions, the number of foreign institutions that were represented (112 universities, 22 laboratories, and 32 others) is impressive and supports the NSLS' reputation as an international research facility.

TECHNOLOGY TRANSFER

Lars Furenlid
NSLS

Technology transfer, the direct collaboration between national laboratories and industry to use both basic research and applied science for technological progress, is now a key mission of the nation's research laboratories. It is formally implemented via Cooperative Research And Development Agreements (CRADAs), in which national laboratory and industry research groups lay out a joint plan of research and shared expenses. For the National Synchrotron Light Source (NSLS), this new mechanism of research contracts complements an already vast range of interactions with industry. This year's Activity Report alone includes approximately 150 abstracts documenting research with industrial involvement.

Technology transfer has been encouraged as standard practice at the NSLS since its inception. The Participating Research Team (PRT) concept, developed at the NSLS in the early 1980's, allows research groups from industry, government and university laboratories to individually or in collaboration build their own beamlines tailored to their specific interests and needs. Twenty-five percent of the beamlines at the NSLS were indeed built by industry, and approximately 400 industrial scientists from almost 70 companies carry out research at the facility. While much of this research is published, approximately 30 companies have signed agreements with Brookhaven National Laboratory allowing them to carry out proprietary research on a full cost recovery basis. Industries also access the NSLS's research resources via the General User proposal system.

Synchrotron radiation is used by industry primarily because it provides advanced analytical capabilities which are not available at the same level or sometimes not even possible at their home laboratories. These capabilities

include probes of vibrational, electronic and magnetic properties such as infrared, photoemission and magnetic circular dichroism spectroscopies; imaging techniques such as computed microtomography, x-ray microprobing, soft x-ray microscopy, topography and x-ray lithography; and structural techniques such as x-ray scattering and reflectivity, single crystal and powder diffraction, and x-ray absorption spectroscopy. What follows are some selected examples of research performed by industrial users during the past year at the NSLS which illustrate the utility of a few techniques. Even this small sampling shows that the facility is providing industry with an impressive array of tools for solving important problems.

X-RAY LITHOGRAPHY

Probably one of the finest examples of industry/national laboratory cooperation is IBM's use of the NSLS to develop x-ray lithography. Over the last decade, IBM has built two lithography beamlines: one to develop the technique and investigate the practical limits of x-ray lithography, and another to address the implementation of this technology on a large scale industrial basis. IBM has transferred images as small as 0.1 micron onto typical silicon wafers. They have fabricated functional, one megabit, dynamic random access memory chips and static ran-

dom-access memory chips with geometries as small as 0.6 microns. Based on their success at the NSLS, IBM has built its own x-ray lithography facility in East Fishkill, New York. It is believed that computer chips with feature sizes down to 0.1 micron can be manufactured using the technique of proximity printing developed by IBM.

A more recent technique in the race to achieve smaller computer chips is being developed on beamline

Figure 1 U13UB: SEM micrograph of 0.075 μm lines and spaces printed in a 60nm thick layer of PMMA on silicon using 6.8 nm radiation. The diagonal mark is a contamination burn mark from the SEM. A.A. MacDowell (AT&T).

U13UB by AT&T Bell Laboratories. They use extreme ultraviolet light (EUV) together with reduction imaging with mirror optics to make features as small as 0.05 μm . A sample pattern printed and etched with this technique is shown in Figure 1. Scientists from AT&T, Sandia National Laboratory and the NSLS are working together to develop large angle collection optics to focus as much as 0.5 to 1 radian of bending magnet radiation onto the pupil of a projection x-ray lithography camera.

PHOTOEMISSION SPECTROSCOPY

Chemical reactions between selected reagents and semiconductor surfaces are another key part of device manufacturing technology. X-ray photoemission spectroscopy, the analysis of the energy and angular distribution of electrons liberated in the excitation of a material by soft x-ray photons, permits the detection of specific chemical species on a surface. Researchers from IBM and Lawrence Livermore National Laboratory, for example, employed the technique on U8B to characterize the products from chemical vapor deposition (CVD) of various methylsilane derivatives on Si(100) and Si(111) as part of a project to develop a technique for growing an atomic layer of C on a silicon substrate. By probing the

C 2s level in the valence band, they can observe the formation of Si-C surface species as molecular precursors, and deposition and annealing conditions are changed.

TOMOGRAPHY

Computed microtomography is conceptually similar to CAT scanning, but it is able to resolve features 1000 times smaller. It is used to observe the inner structure of opaque, heterogeneous materials at micron levels and has been used to study samples as diverse as arthritic human cartilage, catalysts, ceramics, insect bodies and nerve cells. The technique is being developed independently by Exxon, Mobil, and by the Department of Applied Science at BNL. 3D microtomography is conducted by Exxon on beamline X2B as shown in Figure 2. The image preceding Section 2 shows internal channels in a piece of porous sandstone. By determining the structure and connectivity of the channels in a porous rock, and then studying fluid flow, Exxon scientists can test the validity of theories developed to predict fluid flow in the extraction of fossil fuels. In a collaborative effort between IBM and Exxon, the structure of the internal wiring of a ceramic package used to mount integrated circuit chips in mainframe computers was studied to determine the defects in the wiring.

Figure 2 X2B:
John Dunsmuir
(Exxon Research
and Engineering)
developing 3D
x-ray micro-
tomography to
study multi-phase
fluid flow in reser-
voir rock.

Figure 3 X1A: Micrographs of PC/PET blend acquired at a photon energy of 285.36 eV (A) and 285.69 eV (B). High contrast as well as contrast reversal could be achieved with a photon energy change of less than 350 meV. H. Ade and A.P. Smith (NCSU), G. Mitchell and R. Cieslinsky (Dow Chemical)

TOPOGRAPHY

Single crystals or epitaxial layers of silicon carbide (SiC), which is a potentially important wide-gap semiconductor with desirable physical properties for high-power and high frequency applications, typically include a number of defects which are detrimental to device performance. Researchers from Advanced Technology Materials Inc., Cree Research Inc., the U.S. Army Research Laboratory and SUNY Stony Brook have applied white beam x-ray topography on beamline X19C to the characterization of these crystal growth defects. In this technique, the two dimensional intensity distribution in a Bragg reflection is a topograph, i.e. an image of the illuminated crystal surface. Intensity variations reveal the locations and types of defects, some of which can be attributed to particular growth characteristics or presence of impurities which can be dealt with in the production process.

In further interesting applications, Du Pont scientists used topography to characterize growth defects in potassium titanyl arsenate and potassium titanyl phosphate, two promising non-linear optical materials with high laser damage thresholds. Researchers from EG&G imaged mercuric iodide crystals, including samples grown in the microgravity environment of the space shuttle, on X23A3.

MICROSCOPY

Another instrument for which there is rapidly expanding industrial interest is the photoemission microscope. It has a spatial resolution of better than $0.5\mu\text{m}$ and the energy analysis of the emitted photoelectrons gives the instrument both element and chemical sensitivity. The microscope was developed in a collaboration between groups from IBM, Lawrence Berkeley Laboratory, and the State University of New York at Stony Brook on the soft x-ray undulator on X1A. It has been used to study the distribution of metal and metal oxide on chips.

The scanning transmission x-ray microscope, also on beamline X1A, has achieved a breakthrough by combining sensitive chemical contrast with microscopy to distinguish between the components of polymer blends.

Figure 4A U2B: Schematic of the IR microscope/ spectrometer from Spectra-Tech, Inc.

Figure 4B U2B: The infra-red microscope/spectrometer on beamline U2B. Standing from the back: John Reffner (Spectra-Tech, Inc.), Gwyn Williams (NSLS), Larry Carr (Grumman Corporation). Seated: Mary Tungol (FBI).

formed test measurements related to forensic investigations, such as imaging the layers in a cross section of a paint fleck and Polaroid film. Since the material in each layer has a unique vibrational spectrum which can be compared with reference data, the layers can not only be imaged with chemical sensitivity, they can also be identified. The Grumman, Carnegie, and NSLS researchers and their collaborators used the instrument to image defects in semiconductor crystals and films, interplanetary dust particles, and geophysical minerals.

X-RAY SCATTERING

One of the key advantages of utilizing synchrotron x-rays for sample characterization is the ability to select photon energies which can penetrate through windows and environments to reach the desired part of the sample. This permits the design of experiments in which measurements are made *in situ*, i.e. the sample is investigated under the precise conditions of interest. Researchers from AT&T and Rutgers University have developed an *in situ* cell permitting the measurement of surface scattering from Si wafers as they are being etched as part of the device fabrication process. The researchers can monitor

the evolution of the Si surface roughness under a variety of etching conditions by monitoring the width of the scattered peak, and can thus assist in the development of ideal etching prescriptions. Surface scattering is also used by Exxon, IBM, and Hoechst-Celanese researchers to investigate systems ranging from monolayers of organic molecules on clean surfaces to liquid crystals in order to understand surface structures and phase transitions.

Scientists from Dow Chemical and North Carolina State University were able to distinguish between polycarbonate and poly(ethylene terephthalate) microdomains by exploiting the subtle difference in energies of the absorbance peaks associated with pi bond resonances (Figure 3). Researchers from Du Pont and NC State were also able to exploit the linearly polarized characteristic of synchrotron radiation to demonstrate x-ray linear dichroism microscopy, which can further enhance image contrast by separating chemically identical but orientationally different domains.

The U2B infra-red beamline on the VUV Ring was employed as a source for microscopy when Spectra-Tech, Inc. in collaboration with Grumman, the Carnegie Geophysical Institute and the NSLS, installed the infra-red microscope/spectrometer shown in Figures 4A and 4B. The instrument, manufactured by Spectra-Tech, permits collection of spectra on micron size structures, and was used in a number of experiments which amply illustrate its power as an imaging/spectroscopic tool. The FBI per-

Scientists from Du Pont Corporation have together with researchers from BNL begun to apply small angle scattering to the problem of understanding the correlations between production parameters, molecular structure, and properties in nylon fibers. Sample fibers produced with different spinning speeds and heat treatments show a range of polymer properties, such as crystalline and amorphous domain sizes and average interlamellar spacing, which relate to final macroscopic properties. This technique will undoubtedly guide the development of new commercial materials with improved physical characteristics.

POWDER DIFFRACTION

Many solids which can be synthesized via solid state and other techniques, such as the ceramics which make up the majority of the new generation of high T_c superconductors, form powders of microcrystals and resist efforts to grow large single crystals. Their three dimensional structures can still be determined from the diffraction pattern resulting from illumination of the powder.

Figure 5 X3B1: The crystal structure of hydrated sodium aluminate viewed approximately down the c-axis (Na = solid circles, water = open circles).

The random orientation of the microcrystals results in an angular averaging; whereas a single crystal generates a pattern of dots, a powder pattern is a series of concentric rings. Synchrotron x-rays provide significant advantages over conventional laboratory sources: increased peak to background ratios and angular resolution, due to factors such as the high degree of collimation and the high intensity which permits practical discrimination against fluorescence background.

Researchers from Amoco used powder diffraction techniques to solve the structures of catalysts and materials with potential optical applications, such as phosphors

in display devices. These include $\text{BaTiO}(\text{PO}_4)_2$, BaYbF_8 , and $\text{NaAlO}_{2.5} \cdot 4\text{H}_2\text{O}$. The latter structure is shown schematically in Figure 5, and consists of AlO_4 tetrahedra joined together in 4- and 8-membered rings with an interspersal of water molecules and sodium atoms. Du Pont researchers solved the structure of the theta phase of AlF_3 , a catalyst in fluorocarbon transformations.

SINGLE CRYSTAL DIFFRACTION

Many materials which can be obtained in single crystal form are nonetheless challenging or impossible to investigate with laboratory x-ray diffraction equipment because the crystals are too small or subject to x-ray exposure damage. Many large biological molecules fall into this category and the structural biology programs at X12 provide an effective resource for structure determinations of such samples. Researchers from New England Biolabs and Cold Spring Harbor Laboratory recently solved three crystal structures of a DNA methyltransferase, a molecule which recognizes a specific sequence of nucleic acids in a DNA molecule (GCGC) and methylates one of the cytosines. One of the structures, shown in Figure 6, shows the enzyme interacting with a segment of synthesized DNA with the appropriate

sequence. The enzyme binds to the DNA with lobes which interact with the major and minor grooves of the helix. The target cytosine can be seen to swing completely out of the DNA helix to protrude into a cleft in the enzyme where the methylation occurs.

Scientists from the University of Minnesota, North Carolina State University, BNL, and Du Pont Merck have collected single crystal diffraction data on L-subunit ferritin, an iron storage protein, from bullfrog red blood cells. The sample was generated via cloning into *E. coli* and subsequent over expression and isolation. Though the analysis of the high resolution synchrotron data is still

underway, preliminary results indicate a similarity in the overall protein shape to human ferritin, but a significant number of differences in specific loops, helices, and side chains.

The Howard Hughes Medical Institute on beamline X4A specializes in low-energy MAD experiments. Hoffman LaRoche, Inc., in a 5-wavelength/2 anomalous scatterer experiment, studied the cytokine receptor ligand complex which is involved with the immune response system in inflammatory response. Regeneron, Inc., investigated a neurotrophic factor involved in clinical trials for the treatment of Lou Gehrig's disease.

A number of pharmaceutical companies are designing molecules called inhibitors which attach themselves to enzymes and block the action of the disease-causing agents. This approach, called structure-based or rational drug design, relies on knowledge of the enzyme structure as well as the interaction of the enzyme with the inhibitor. The Structural Biology Center on beamline X8C has attracted a number of pharmaceutical companies, most of which are conducting proprietary research. Eli Lilly and Company, SmithKline Beecham Pharmaceutical, and Glaxo, Inc. are studying Phospholipase A2 in order to design treatments for inflammatory diseases. Merck & Co., Inc., is investigating human recombinant Inositol Monophosphatase, which is the putative lithium target for the treatment of depression. Both SmithKline Beecham Pharmaceutical and Monsanto are collecting data on the HIV protease associated with AIDS. Monsanto is also studying human Renin and Class II Major Histocompatibility protein DR4-DW4 in order to devise treatments for hypertension and rheumatoid arthritis, respectively. Other companies utilizing the X8C beamline include Bristol-Myers Squibb, Procter & Gamble, Sterling Winthrop, and Abbott Laboratories.

TRANSVENOUS CORONARY ANGIOGRAPHY

The transvenous digital subtraction coronary angiography project at the NSLS has obtained research quality images of human coronary arteries. It was initiated at Stanford University and the Stanford Synchrotron Radiation Laboratory and now operates at the NSLS. The project goal is to develop a technique for obtaining images of the human coronary arteries by means which are safer for patients than conventional imaging (see images preceding Section 1 of this Activity Report). Collaborators now include physicians from Stanford University, North Shore University Hospital and the Health Sciences Center at SUNY-Stony Brook as well as physicists from Lawrence Berkeley Laboratory, Stanford University, the European Synchrotron Radiation Facility, and the NSLS.

The present image acquisition and processing system limits the real-time information available to the physicians. In addition, the imaging sessions are restricted to periods of time when the storage ring is operating near its maximum stored current. These limitations can be overcome by utilizing a real-time image visualization and processing system coupled with a new x-ray source with higher flux. In April 1993, the NSLS and Advanced Acoustic Concepts, Inc. (AAC) began discussions concerning a collaboration to develop such an image acquisition, processing, and display system. This is the first year of a proposed two-year program to incorporate technology which is unique to the Acoustic Intercept Screener Processor System (AISPS) developed by AAC for the U.S. Navy. NSLS personnel will develop the necessary insertion device for enhancing the x-ray source at the synchrotron.

Figure 6 X12C: Stereo drawing of α -carbon backbone of the M.HhaI and the bound duplex DNA. The target cytosine has swung out of the double-stranded DNA helix (shaded areas). X. Cheng, S. Kilmasauskas (Cold Spring Harbor Laboratory) and S. Kumar, R. J. Roberts (New England Biolabs).

X-RAY ABSORPTION SPECTROSCOPY

The advantages of x-ray spectroscopy as a research tool are, of course, the ability to selectively study specific elements and their chemical environments, and to probe either surfaces or internal volumes of materials in systems with or without long range order. The sample can be solid, liquid, or even gaseous; at any temperature; at any pressure; and subject to any variety of conditions limited only by the experimenter's ingenuity. When combined with the large number of photons which beamlines can deliver to a sample ($> 10^{10}$ - 10^{12} monochromatic photons/second), this technique is a uniquely powerful tool for investigating an element's charge state and local structure, i.e., what atoms surround the element and at what distances.

Near edge spectroscopy, the examination of the fine structure in the area of the spectrum at an element's absorption edge, can also be used as a fingerprinting technique to quantify the relative amounts when an element appears in more than one form. The technique is quite sensitive: surface species can be measured at submonolayer coverages, whereas bulk experiments can give acceptable edge statistics with concentrations > 10 ppm. The applications germane to problems of industrial interest are virtually limitless and, indeed, practically all physical and life sciences, as well as many engineering fields, are represented on the experimental floor.

Researchers from Exxon studied the x-ray absorp-

tion edges of different sulfur-containing compounds found in crude oil and coals, some of which can foul combustion chambers and contribute towards acid rain. Exxon, Mobil, Chevron, Du Pont, Dow Chemical, BP America, and Monsanto are among the corporations that have been studying catalyst systems including zeolites, metal colloids and silica-supported metals. The chemistry of many experimental and commercially employed catalysts is not well understood, and even a small improvement in efficiency for a large scale process can result in big economic gains. Among the interesting recent experiments are structural studies of transition metals incorporated into the AlSi frameworks of certain zeolites in the hope of modifying their chemical properties. Figure 7 shows researchers from Dow working at beamline X19A.

Several companies active at the NSLS are involved in the remediation of trace metals released into the environment. XAS measurements help to identify the specific chemical form of potentially toxic metals, for example, U, Pb and Cr in soils, in order to guide the design of an effective cleanup procedure. Principal government and corporate research groups are from Du Pont, Westinghouse Savannah River Company and the Naval Research Laboratory. The Du Pont group recently concluded that environmental Pb generally exists as relatively inert sulfides or sulfates as long there is sufficient S available, and that addition of sulfide can be a strategy for remediating existing sites with contaminated soils.

Figure 7 X19A:
Dow researchers
Joseph Maj (left) and
Simon Bare (right)
setting up a
fluorescence
experiment in the
X19A hutch.

Figure 8: Fourier transforms of EXAFS spectra measured normal and parallel to the plane of a FeTb thin film used in magneto-optic devices. V. Harris and T. Elam (NRL) working on beamline X23B, discovered that the material's ability to store data at very high densities results from structural anisotropy (as shown by the difference between the solid and dotted lines).

The semiconductor and communications industries also benefit from synchrotron techniques and technology transfer. AT&T Bell Laboratories pursues a wide

CONCLUSION

This discussion of industrial research at the NSLS is, of course, flawed as it is only a cursory survey of published research and makes no accounting of proprietary work. Furthermore, secondary contacts undoubtedly exist between academic, governmental, and industrial programs which make use of research based at the NSLS, but are not reported back to the facility. The lists of corporations and government agencies performing research at the NSLS, see Tables A and B*, are impressive indications of the extent to which synchrotron techniques are impacting on industrial research and development efforts.

array of research topics at several beamlines. Both AT&T Bell Laboratories and Bellcore, for example, have been investigating Er doped optical fibers, a promising new technology for creating fiber amplifiers in the 1.55 mm telecommunications window. The AT&T Bell Labs group was able to demonstrate with XAS measurements that the widely different luminescent intensities observed from Er in different grades of Si resulted from the Er ion coordinating twelve Si atoms in pure Si, versus six O atoms in Si with significant O content. This information will be crucial in the drive to produce devices from this technology, perhaps the first steps in a revolution in fiber optics communications and optical computing.

Recent work by researchers from the Naval Research Laboratory on amorphous TbFe films used in magneto-optical storage devices for computers provides yet another example of the potential impact on an industrial technology by research conducted at the NSLS. The key feature of these materials is their intrinsic magnetic anisotropy: the magnetization direction is maintained perpendicular to the plane of the film, thereby permitting very high bit storage densities. The exact cause of this effect was unknown until the NRL group was able to demonstrate that the magnetic anisotropy is a consequence of structural anisotropy. The distribution of nearest neighbors, measured with polarization dependent XAFS, was found to be different in the directions parallel and perpendicular to the plane of the film. An annealing process which attenuated the magnetic anisotropy unambiguously demonstrated the correlation by also decreasing the measured structural anisotropy. Further investigations demonstrated that the degree of structural and magnetic anisotropy can be varied by adjusting the temperature of the substrate during fabrication via deposition. The fundamental understanding of the relationship between processing conditions, structure, and magnetic behavior in these materials are already guiding the development of the next generation of high density storage devices (Figure 8).

Providing access to sophisticated experimental hardware via formal or informal research collaborations is only one aspect of the NSLS's service to the commercial sector. Perhaps the most important technology transfer occurs in the exchange of ideas that takes place every day on the NSLS floor among scientists from a myriad of institutions.

* Based on active users as of April 1994.

Table A: U.S. Corporations

AT&T Bell Labs	Lawrence Associates, Inc.
Aerospace Corporation	Merck & Co.
Air Products Corporation	Miles, Inc.
AlliedSignal, Inc.	Mission Research Corp.
Amoco Corporation	Mobil R&D Corp.
Applied Physics Technologies Corporation	Monsanto
BP America	Motorola
Bio-Imaging Research, Inc.	Moxtek, Inc.
Biosyn Technical, Inc.	NEC Corporation
Bristol-Myers Squibb	Nicolet Instrument Corporation
Chevron Research & Technology Company	Physical Sciences, Inc.
Corning, Inc.	Polaroid Corporation
Deltronic Crystal Industries	Princeton Instruments
Dow Chemical	Proctor & Gamble Co.
DuPont Merck Pharmaceuticals	R&D Services, Prop.
E.I. DuPont de Nemours Co.	Radiation Science, Inc.
EG&G Energy Measurements	Rockwell International
Eastman Kodak Co.	Sachs Freeman Associates, Inc. (SFA)
Eli Lilly and Company	Schlumberger-Doll
Engelhard Corporation	Science Applications International Corp.
Enraf-Nonius, Inc.	Siemens Analytical X-ray Institute
Exxon Research and Engineering Co.	SmithKline Beecham Pharmaceuticals
Frequency Electronics, Inc.	Spectra-Tech Inc.
GTE Labs	Superconductor Technology, Inc.
Genencor International	Sylvania, Inc.
Genentech, Inc.	Texaco Research Center
General Motors Research Labs	The EXAFS Company
Glaxo, Inc.	UOP
Grumman Aerospace	Upjohn Co.
Hoechst Celanese Research Corp.	Westinghouse Savannah River Co.
Hoffmann-La Roche	X-ray Analytics, Ltd.
IBM Research Division	X-ray Optical Systems, Inc.
Kraft General Foods	

Table B: U.S. Laboratories and Government Agencies

Laboratories

The Scripps Research Institute
Ames Laboratory
Argonne National Laboratory
Brookhaven National Laboratory
Cold Spring Harbor Laboratory
Fred Hutchinson Cancer Research Center
Geophysical Laboratory
Lawrence Berkeley Laboratory
Lawrence Livermore National Laboratory
Los Alamos National Laboratory
Oak Ridge National Laboratory
Pacific Northwest Laboratory
Sandia National Laboratory
Savannah River Ecology Laboratory
Stanford Synchrotron Radiation Lab

Government Agencies

Army Research Laboratory
Federal Bureau of Investigation (FBI)
National Aeronautical Space
Agency (NASA)
National Institute of Standards and
Technology (NIST)
Naval Research Lab (NRL)
Naval Surface Warfare Center
Plum Island Animal Disease Center
U.S. Air Force
U.S. Army
U.S. Geological Survey

ATOMIC AND MOLECULAR SCIENCE

Mei-Ling Shek

NSLS

I VALENCE ELECTRONIC EXCITATION

The research programs on beamline U11, which is dedicated to gas phase molecular studies involving valence electronic excitations, include photoionization-induced intracuster reactions and thermochemistry in Van der Waals complexes, photoionization of radicals, and studies on the formation of ions and ion pairs due to the photodissociation of small molecules.

To understand the dynamics of the dissociative photoionization of the Van der Waals mixed trimer $(C_6H_6)_2O_2$ to produce $C_6H_6O^+$ (see the 1991 NSLS Annual Report), the kinetic energy releases of the production have been measured, as shown in Figure 1. The mean energies are found to be those expected for the unimolecular decay of excited $(C_6H_6)_2O_2^+$, and nonstatistical processes are not important. Studies on chlorobenzene/ammonia complexes also do not reveal any significant nonstatistical processes in their ion productions by photodissociation.

Figure 1 U11: Distribution of kinetic energy releases in the center-of-mass system for $C_6H_6O^+$, produced at wavelengths 750 Angstroms (16.5 eV) and 600 Angstroms (20.7 eV), are given by solid lines. The distribution of kinetic energy release for $(C_6H_6(O_2))^+$, produced at a wavelength 700 Angstroms (17.7 eV) exclusively from the neutral dimer $C_6H_6(O_2)$, is given by the dashed line, and has an apparent energy distribution determined only by the beam temperature and instrumental resolution. J.R.Grover (BNL Chemistry), E.A.Walters (U. of New Mexico), and B.-M.Cheng (SRRC,Taiwan).

A method has been developed to obtain the controversial dissociation energy $C_6H_6 \bullet Ar \rightarrow C_6H_6 + Ar$, by subtracting the ionization potential for $C_6H_6 \rightarrow C_6H_6^+$ from the appearance potential for $C_6H_6 \bullet Ar \rightarrow C_6H_6^+$. In addition, in the study of benzene-Ar complexes, sharp features in the photoion yield curves of $(C_6H_6)_m Ar_n^+$ can be observed, owing to Penning ionization from excited Ar^* ($3p^6 \rightarrow 3p^5 4s$) in the cluster. Cluster dissociation energies have also been determined for $C_6H_6 \bullet H_2O$, which is a prototype for a theoretical understanding of hydrocarbon-water interactions. Similarly, the thermochemistry and energetic relationships in perfluoroethylene/oxygen systems have been established with threshold measurements, and are given in Figure 2; such studies may lead to an understanding of the solubility of oxygen in liquid fluorocarbons.

The photoion yield threshold determination of the adiabatic ionization potential of the $BrO(X^2 \Pi_{3/2})$ radical,

Figure 2 U11: Energy relationships (in eV) in the C_2F_4/O_2 system of mixed Van der Waals complexes. B.-M.Cheng (SRRC,Taiwan), J.M.Preses (BNL Chemistry), and J.R.Grover (BNL Chemistry).

generated by reacting Br_2 with atomic $O(^1P)$, is shown in Figure 3. The only other determination of the ionization potential of BrO was from photoelectron spectroscopy, which suffered from interferences by photoelectrons arising from various photo-excited oxygen and bromine species.

II SOFT X-RAY INDUCED CORE ELECTRONIC EXCITATION

The high flux and high energy resolution at U13UA make it possible to achieve state-selective, chemical site-specific core level excitations to study the dynamics of core hole excitation and de-excitation processes in small molecules. On U15, an experiment has given evidence for interchannel coupling of core and valence photoionization. On X1B, satellites in the C 1s photoelectron spectrum of benzene can be studied in detail.

The resonance Auger spectra of the carbonyl C in methyl formate, propionaldehyde and acetone, obtained by high resolution photon excitation at 286.3 eV to select only the carbonyl C $1s \rightarrow \pi^*$ transition, are shown in Figure 4. The similarity in peak energies and intensity ratios demonstrates that the resonance Auger spectra are specific to the chemical site.

The photofragmentation of methane has been studied by tuning the photon energy to different excited $1s$ hole states, including the dipole-forbidden $1s \rightarrow 3s(a_1)$ excitation observable on U13UA (see the 1992 NSLS Annual Report for the resonance Auger spectra induced by such selective core level excitations). Some systematic differences are found when compared with valence excitation and C 1s excitation to the continuum. The fragmentation patterns of a homologous series of chlorinated hydrocarbons have been obtained by selective Cl L-shell resonance excitation and

continuum excitation. The fragmentation patterns for excitation above the Cl L₁ edge are shown in Figure 5. The effects of charge delocalization by the carbon chains on the Cl core hole decay are seen in the decreasing yield of Cl^{++} and Cl^+ with increasing number of carbon atoms. Together with the detection of ions in coincidence, the factors for C-Cl bond breaking can be studied.

On U15, the photon energy dependence of the N_2^+ ion yield, following K-shell excitation of N_2 , is found to be reflected not only in the energy dependence of the luminescence yield due to the removal of the $2\sigma_u$ valence electron, but also in the $2\sigma_u$ photoelectron yield. The branching ratios for the processes leading to N_2^+ produc-

Figure 6 X1B: The C 1s photoelectron spectrum of benzene at photon energies 300.7 eV and 308.5 eV, showing the photoelectron main peak and well-resolved shake-up satellites which have different relative intensities at different photon energies. Different angular distributions for the individual satellites have also been observed. H.M.Koepppe, B.S.Itchkawitz, J.Feldhaus and A.M.Bradshaw (Fritz-Haber Institute, Berlin).

tion, namely, interchannel coupling, x-ray fluorescence, and resonance Auger decay, can be determined.

On X1B, measurements have been made of the C 1s main photoelectron peak and the first group of shake-up satellites in benzene, in the photon energy region between threshold (290.4 eV) and 350 eV. This work aims at understanding the origins of the C K-edge features in the photoabsorption of benzene, and their effects on various ionization channels. The spectra in Figure 6 show the different satellite intensities at different photon energies.

III ATOMIC PHOTOIONIZATION

The double ionization of He by photoabsorption continues to generate great interest, since this provides a sensitive test for an understanding of electron-electron correlation. Previous measurements on the ratio of the cross-sections for double to single ionization, done by Levin and co-workers on X24A and X26C (see the 1991 and 1992 NSLS Annual Reports), have been re-examined by Bartlett and co-workers on X8A. It is suggested that ionization due to Compton scattering, omitted in previous interpretations, becomes significant at photon energies above 3.7 KeV and dominates the ratio in the energy range 8.2 to 11.6 KeV. The results of Bartlett and co-workers are shown in Figure 7 and fair agreement is observed with the calculation of Andersson *et al.* which includes the effects of Compton scattering.

The satellite structure in the Ar 1s photoelectron spectrum has been obtained at X24A. The satellite structure shows a remarkable similarity with the Ar K photoabsorption suprathreshold structure. The latter has been interpreted to arise from final ion states (hole vacancies 1s3p, 1s3s, 1s3p²) with excited valence electrons.

Figure 7 X8A: The ratio of the cross-sections for double to single ionization of He by photoabsorption, between 2.1 to 5.5 KeV, and a comparison with calculation (dashed curve) including Compton scattering. R.J.Bartlett (Los Alamos National Laboratory), M.Sagurton (SFA) and J.A.R.Samson (U. of Nebraska).

ENERGY DISPERSIVE DIFFRACTION

Syed B. Qadri
Naval Research Laboratory

Energy dispersive diffraction techniques at the NSLS are used mainly in obtaining diffraction information from samples whose volume ranges from a few nanoliters to a few attoliters, such as with specimens contained in diamond-anvil cells (DAC) or encapsulated in glass capillaries. In the case of diamond-anvil pressure cells, extreme static pressures are generated within a region of only a few tens of microns between the culets of a pair of opposed diamond anvils. Pressures have been reached exceeding that at earth's core, ~360 GPa. Moreover, because of the small volume of the sample and the good thermal conductivity of diamond, the DAC can be readily cooled to cryogenic temperatures or heated to temperatures in excess of 1000 K. Most of the energy dispersive diffraction research this past year was performed using beamline X17C.

Kingma and co-workers from Carnegie Institution of Washington (CIW) demonstrated that samples recovered from static compression experiments of α -quartz exhibit an unusual pressure-induced microstructure, which arises from a new phase transformation at 21 GPa. Upon decompression they found that the high-pressure phase reverts to a quartz like structure in a twinned state, accounting for the previously reported elastic behavior. Figure 1 shows their data on interplanar spacings and representative energy-dispersive synchrotron x-ray diffraction spectra of polycrystalline α -quartz [see K.J. Kingma *et al.*, Phys. Rev. Lett. **70**, 3927 (1993)].

Vos and co-workers from CIW performed experiments on H_2 - H_2O mixtures. For the first time, a molecular mixture containing water to high pressures was studied in excess of 2.0 GPa and two new hydrogen hydrates C_1 and C_2 have been discovered. The C_1 structure should also be favorable for small molecules such as helium and neon, because both C_1 and C_2 have higher melting temperatures than pure ices at the same pressure. Clathrates are of considerable importance to planetary interior layers of H_2 -He and ice where high pressures and temperature prevail [see Vos *et al.*, Phys. Rev. Lett. **71**, 3150 (1993)].

Figure 1 X17C: Interplanar spacings (left) and representative energy-dispersive synchrotron x-ray diffraction spectra of polycrystalline α -quartz (right) as a function of pressure. Kingma *et al.*, Phys. Rev. Lett. **70**, 3927 (1993).

Loubeyre and co-workers from the University of Paris, in collaboration with Mao *et al.* from the CIW, studied the equation of state of 4He to 58 GPa over the temperature range of 46-500K. The hcp structure is stable, apart from an fcc loop which occurs along melting between 15K and ~285K. Their comparison of the 304K hcp equation of state with a series of calculations demonstrates that there are significant attractive many-body interactions. Figure 2 shows volume versus pressure data of hcp 4He at 304 K along with a comparison with four calculated equations of state. This is believed to be the highest pressure at which single crystal measurements have been carried out [see P. Loubeyre *et al.*, Phys. Rev. Lett. **71**, 2272 (1993)].

Akella and co-workers studied the structural phase transformations in lanthanides and actinides as a function of pressure to 300 GPa at room temperature. They reported that with the exception of Ce and Pr, no large volume changes were noticed from these metals as they went through several phase changes. They indicated that the appearance of a bct ultra-high pressure phase in Ce, Sm, Th and possibly in Np, raises the possibility that the ultimate high pressure structure for the 4f and 5f metals may be the bct structure.

Vohra and co-workers (U. of Alabama) and S.S. Vagarachi (General Electric Abrasives) used isotopically pure (isopure) ¹²C diamonds in their diamond anvil cell. They achieved a calibrated static pressure of 250 GPa as measured by x-ray diffraction using synthetic diamonds. Jun Liu and Vohra also studied the pressure dependence of fluorescence spectra of a Sm-doped YAG optical pressure sensor up to 73 GPa. X-ray diffraction studies show that the cubic phase of YAG crystal is stable to 69.0 GPa (Figure 3) and the volume compression is 17.9%. The increase in the fluorescence intensity of the Sm:YAG with increasing pressure has practical applications in ultra high pressure/high temperature research [see J. Liu and K. Vohra, *Solid State Commun.* **88**, 417 (1993)].

Skelton and associates from the Naval Research Lab (NRL) and CIW have studied two high-temperature superconductors, YBa₂Cu₃O_{7-δ} and Nd_{2-x}Ce_xCuO_{4-y}, for evidence of structural inhomogeneities. By illuminating the samples with a highly collimated x-ray beam produced on X17C, small changes in the c-axis lattice parameters were detected over a spatial scale of 10 μm. These changes are interpreted as evidence of variations in the oxygen

content in YBa₂Cu₃O_{7-δ} and cerium content in Nd_{2-x}Ce_xCuO_{4-y}, both of which affect the superconducting properties. This is the first example of detecting structural variations directly on a spatial scale of this size. Figure 4 shows the variation of the oxygen parameter (7-δ) and c-axis parameter of YBa₂Cu₃O_{7-δ} as a function of the positional coordinates. (This work has been accepted for publication in *Science*, 1994.)

Qadri and co-workers from NRL in collaboration with CIW studied a number of II-VI semiconducting compounds and their ternary compounds at room temperature. Two new phases of ZnTe were discovered including a cinnabar phase at 10.0 GPa. Compressibility data were also collected on several of the new Hg-Ba-Ca-Cu-oxide superconductors. This information was used to convert data from dT/dP measurements performed at NRL into dT/dV values.

LITHOGRAPHY MICROSCOPY AND TOMOGRAPHY

G. P. Williams

NSLS

X-RAY FLUORESCENCE MICROPROBE

The x-ray fluorescence microprobe (XRM) at beamline X26A was used in a wide variety of applications in scientific fields ranging from plant physiology to extraterrestrial materials. Instrumentation innovations included the successful use of the microbeam (1.3 μm diameter) produced by a tapered glass capillary (S. Hoffman, CHESS) for trace element analysis and mapping, and the commissioning of a new 13-element Ge detector capable of full spectral acquisition in each channel. Three applications are highlighted here:

Selenium Mobility Experiments in Sediments: T. Tokunaga (LBL), S. Sutton and S. Bajt (U. of Chicago). Selenium geochemistry in soil environments is being studied to aid remediation of soils contaminated with seleniferous agricultural drain waters, such as those at Kesterson Reservoir, CA. Laboratory simulation experiments were performed at LBL with Se-uniform starting sediments. The XRM work demonstrated that Se is mobilized to anaerobic microsites adjacent to decaying plant roots (Figure 1), which may explain the observed slow re-oxidation of Se in these systems.

Microbeam Determinations of Iron Oxidation State: J. Delaney (Rutgers U.), S. Bajt and S. Sutton (U. of Chicago). Work is in progress to develop microbeam techniques for determining the oxidation state of iron using x-ray absorption near edge spectroscopy (XANES). Fe oxidation state is of fundamental interest to earth and planetary scientists primarily because Fe-dominated phase relations are important geochemical controls under the reducing conditions that exist in planetary interiors. The energy shift of the Fe K pre-edge peak is approximately a linear function of oxidation state for well-characterized standards such as hematite (Fe^{3+}), magnetite $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+}) = 0.67$ and fayalite (Fe^{2+}). Using this calibration relation, a suite of altered magnetite test samples yielded Fe^{3+} concentration: qualitatively consistent with estimates based on electron microprobe analyses and x-ray powder diffraction. This technique may eventually be useful for determining the oxygen fugacity of igneous

systems, thereby providing key information on planetary evolution.

Volatile Trace Element Depletions in Micrometeorites: G. Flynn (SUNY-Plattsburgh) and S. Sutton (U. of Chicago). Micrometeorites collected from the stratosphere are being studied to determine the compositions of the zodiacal cloud, comets and asteroids. The degree of heating during atmospheric entry can be used to identify particles originating from comets and asteroids. Zn

Figure 1 X26A: Synchrotron x-ray fluorescence microprobe map of the selenium distribution in a water-saturated sediment and decomposing root of *Scirpus*, a common wetland plant. The 5x5 mm image shows Se concentration, with a maximum value of about 3800 mg/kg. Prior to decomposition, Se was initially homogeneously distributed as selenate [Se(VI)] at a concentration of 70 mg/kg.

The Se map shows a locally dramatic increase in the total Se concentration adjacent to the root, supporting the hypothesis that soluble Se(VI) was reduced to the less mobile Se(IV) and insoluble Se(0) in the region of higher microbial activity. Such small-scale Se heterogeneity may significantly influence the susceptibility to Se remediation. T. Tokunaga (LBL), S. Sutton and S. Bajt (U. of Chicago).

depletions determined by the XRM were found to be correlated qualitatively with other heating indicators, notably, development of magnetite rims (by TEM) and He loss (by mass spectrometry). A quantitative thermometer based on Zn content is being pursued.

The X26A microprobe was also used for other pioneering studies of materials including hydrothermal fluid inclusions (Georgia State U. and Virginia Polytechnic Institute), wheat roots (Purdue U.), carbonates (SUNY-Stony Brook), bone (BNL DAS), lunar rocks (U. of Chicago), ancient Chinese bronzes (SUNY-Stony Brook and BNL Metallurgy), as well as various studies of elemental partitioning in geochemical systems.

X-RAY MICROSCOPY

The X1A scanning x-ray microscope can image wet or dry specimens at atmospheric pressure, and provide elemental and chemical information at a resolution that is at least five times better than that obtained with a visible light microscope. The microscope was built primarily with biological imaging in mind and most of the work is in this area, an example being shown in Figure 2. How-

ever, there have been some very interesting developments involving other applications:

Chromosomes; S. Williams, *et al.* (SUNY -Stony Brook). Chromosomes are too small to study in detail by visible light microscopy and too thick to view in the conventional electron microscope without unwinding or sectioning. Using the X1A scanning x-ray microscope to study chromosomes, Shawn Williams' (BNL Biology) first findings [Williams *et al.*, *Journ. Mic.* **170**, 155 (1993)] demonstrate that wet chromosomes are morphologically altered by drying processes used for electron microscopy. Furthermore, it appears that the scanning microscope can collect the information from each pixel fast enough (in a few milliseconds) that radiation damage does not have time to corrupt the image. These findings were utilized in an x-ray microscope study which compared the morphology and composition of chromosomes from a variety of plant and mammal species. This early work suggests that the protein-to-DNA ratio of metaphase chromosomes is independent of species and the amount of DNA per chromosome, implying a common mode for DNA packaging.

Luminescence microscopy; C. Jacobsen, *et al.* (SUNY-Stony Brook). The goal of the luminescence microscopy work at beamline X1A is to extend the resolution of the visible/UV fluorescence microscope by at least a factor of five. Conventional fluorescence microscopy is based on the availability of dyes which emit light when hit by UV photons. In addition, dye luminescence can also be stimulated via energetic electrons, such as those created following soft x-ray absorption. These dyes can be attached to molecules which, by immunological mechanisms, seek out targets of particular interest in biological specimens. Such specific labeling has become a powerful tool in cellular biology, even though the resolution of the available visible light microscopes is limited to $0.2\mu\text{m}$. The spatial resolution of the luminescence microscopy at X1A should be determined by the size of the focused soft x-ray beam, $\sim 300\text{\AA}$. The first tests at X1A by C. Jacobsen, *et al.*, with phosphor grains and dye-loaded spheres, demonstrated the validity of the idea (Figure 3). To achieve specific labeling, it will be necessary to develop the

Figure 2 X1A: Life cycle of the blood stage of malaria as viewed by x-ray microscopy. Red blood cells infected by the parasite that causes malaria were first studied using x-ray microscopy by M. Moronne and collaborators (LBL). The images shown here were taken by W. Mangel, W. McGrath, and S. Williams (BNL Biology) as part of an ongoing study aimed at confirming or disproving confocal fluorescence microscope studies suggesting the existence of a duct connecting the surface of the parasite within the red blood cell to the surface of the red blood cell. This is an important project because if the duct exists (the original experiments have not been confirmed), then a drug therapy based upon surface antigens of the parasite within the red blood cell should be considered. 400 million people have malaria now, and 1 million of them will die this year (mostly children).

Figure 3 X1A: Dye-loaded polystyrene spheres viewed using scanning luminescence x-ray microscopy. These first studies pointed the way to the development of luminescence as a way to tag sites of specific biochemical activities. See C. Jacobsen, S. Lindaas, S. Williams, and X. Zhang, *J. Microscopy* **172**, 121 (1993).

right combination of dye molecules and immunological labels. Promising steps along this direction are being taken by a group from LBL (Moronne, Glaeser, *et al.*), and form a major component of their proposal for a microscopy facility at the ALS.

Near Edge X-ray Absorption Fine Structure (NEXAFS) microscopy: H. Ade, *et al.* (NCSU). NEXAFS spectra are characteristic of the chemical bonding and coordination of atoms in a wide variety of samples. With scanning transmission x-ray microscopy, it is possible to record NEXAFS spectra from specimen areas of 0.2 μm or less. Having determined the photon energies most characteristic of a chemical component of interest, one can then acquire images at these energies to map its distribution. This was demonstrated by application to polymer blends [Ade *et al.*, *Science* **258**, 972 (1992)], where the ability to differentiate between the various components is of particular value in assessing polymer morphology. One of the strengths

of NEXAFS microscopy is its ability to identify and characterize production problems in polymer products. These include detrimental precipitates and impurities where visualization of the morphology alone (which could be achieved in electron microscopes with the use of stains), is of relatively little value. Identification of chemical composition is also of great value in assessing the micro-chemistry and micro-heterogeneity in coal (G. Cody, *et al.*, *Energy and Fuels*, in press). Even in the complex environment of biological structures, NEXAFS imaging can be used to differentiate between components such as protein and DNA, as demonstrated by X. Zhang, *et al.* (SUNY-Stony Brook). NEXAFS imaging has been further developed by making use of the linear polarization of the x-ray

beam to map the orientation or alignment of specific functional groups of a polymer. This has been demonstrated recently at beamline X1A in the case of a Kevlar fiber (Figure 4), establishing a preferentially radial alignment of the benzene rings relative to the fiber axis [H. Ade and B. Hsiao, *Science* **262**, 1427 (1993)].

Figure 4 X1A: Micrographs of a 200 nm thick Kevlar 149 fiber section (cut at 45° to the fiber axis) imaged with the electric field vector in the left-right (on the left) and up-down (on the right) direction at a photon energy of 285.5 eV. This energy selects the aromatic group of the fiber polymer and the butterfly patterns are due to the radial symmetry and the orientational order of the fiber. The observed linear dichroism in these images is confirmed by the contrast changes between the two images.

Figure 5 X2: X - R a y tomograph image of a sample of Fontalnbleu sandstone showing the pore geometry. The image is a 480 μ m cube, with 64 voxels (volume pixels) along each edge. The full volume data are used in transport models used to calculate porosity, permeability and formation factor. J.H. Dunsmuir, J.H. Hardenberg and B.P. Flannery (Exxon).

X-RAY TOMOGRAPHY

This past year has seen a continuing development of the x-ray microtomography facility at X2. Dunsmuir, Hardenbergh and Flannery (Exxon) have done extensive work on characterizing several diverse examples of porous media which include oil reservoir materials (Figure 5), micromachines and the cardio-vascular trees of rodent hearts.

INFRA-RED MICROSCOPY

Recently, infrared (IR) microscopy has been developed at the VUV Ring in a collaboration involving J. Reffner (Spectra-Tech, Inc.), L. Carr (Grumman Corporate Research Center) and the NSLS, with participation by S. Sutton (U. of Chicago) and C. Meade (Carnegie Inst. of Washington). A powerful advantage of IR microscopy is that there are many vibrational modes in the IR spectral range, which provide a unique chemical fingerprint for each compound. The brightness

of the NSLS VUV Ring makes it an ideal candidate for this application, and the recent development of a new infrared extraction port at U2B afforded an ideal opportunity to test its applicability. The present experiments were performed in the near to mid IR (2-15 microns or 650-5000 cm^{-1}). In the initial tests of the installed microscope, it was found that most of the flux from the NSLS could be passed through a 10 μ m aperture. This is consistent with what would be expected for a 1mm beam size demagnified by a factor of 100 on going from $f/100$ optics to $f/1$ optics. The flux provided by U2B is also significantly better than that obtained using a conventional black-body source (one of which is provided with the instrument): in order to obtain the same signal from the black-body, the aperture had to be increased to 100 μ m. Therefore, the source enhancement factor is around 100. In addition, the greater stability of the synchrotron source produces lower-noise spectra than the black-body.

Figure 6 U2B: Cross-section of the active layer of a piece of photographic film, with the 6 μm outermost layer of gelatin at the top and traces of the backing paper appearing as the flake-like material at the bottom. The layers adjacent to the gelatin are three different mixtures of polyvinyl acetate and polyvinyl alcohol of thicknesses 4, 4 and 8 μm . The thicker (32 μm) layer adjacent to the paper is polyethylene. J. Reffner (Spectra-Tech, Inc.).

Figure 7 U2B: Absorption spectra taken with approximately 10 μm spatial resolution in 1 μm steps running across the series of layers of the photographic film cross-section in Figure 6. The outside surface is in the foreground. The peaks correspond to the characteristic vibrational modes of the constituent molecules, providing easily-distinguishable chemical signatures of the various layers. The outermost layer is gelatin, the following three layers are different mixtures of polyvinyl acetate and polyvinyl alcohol, and the thick layer is polyethylene. J. Reffner (Spectra-Tech, Inc.).

Photographic Film Emulsion: J. Reffner (Spectra-Tech, Inc.). In the first test of the U2B microspectrometer, J. Reffner measured the sample shown in Figure 6, which is a cross-section photograph of a photographic film

emulsion. Five layers can be seen, with thicknesses 6, 4, 4, 8 and 32 μm . Figure 7 shows a series of IR absorbance spectra in the 600-4000 cm^{-1} range taken across the layers of the film at intervals of 1 μm . The chemical signatures of the various layers are easily visible.

Figure 8 U2B: Absorbance maps of a 200µm × 200µm area on the surface of a Cd(Zn)Te crystal at wavelengths of (a) 3µm and (b) 8µm. The pixel size is 20µm. Darker squares indicate locations of higher absorption. The structure in the images indicates that contrast can be obtained in the IR region, thus offering the capability of mapping inhomogeneities in the physical constants of materials. L. Carr (Grumman Corporate Research Center).

Defects in Semiconductor Materials; L. Carr (Grumman Corporate Research Center). Defects strongly affect the electrical and optical performance of semiconducting materials. For example, CdTe is an important substrate for many II-VI compound semiconductor devices and IR electro-optic modulators. Absorbance maps of a Cd(Zn)Te crystal measured at 3µm and 8µm wavelengths are shown in Figure 8. The defect which appears in the upper left-hand corner of both maps is probably a region with high dislocation density. Another defect along the left edge appears only for the 3µm wavelength, which suggests a tellurium precipitate. Other IR microspectroscopy measurements were performed on $Hg_{1-x}Cd_xTe$ alloy epilayers to determine the bandgap energy. Improper material growth conditions can lead to variations in this value with position and, ultimately, device failure.

Interplanetary Dust Particles; S. Sutton (U. of Chicago). The compositions, mineralogy and textures of 10µm interplanetary dustparticles (IDPs), which are micrometeorites collected in the stratosphere, are of interest in understanding the evolution of solar systems. This work involves a collaboration between planetary scientists at the U. of Chicago and MVA, Inc. (Norcross, GA). Figure 9 shows the IR absorption spectrum from one of these micrometeorites. The width and shape of the Si-O band near 1000cm⁻¹ is consistent with the dominant silicate mineral being pyroxene ([Ca,Fe,Mg]SiO₃) rather than olivine ([Fe,Mg]₂SiO₄) or hydrated phyllosilicate. Future work will attempt to analyze micrometeorite subunits, some of which have been hypothesized to be of interstellar origin.

Mantle Silicates; Another important application of synchrotron IR microspectroscopy is the study of the high pressure phases of microscopic samples, both at atmospheric and at high pressure (using *in situ* diamond-anvil cells). These include studies of IR-active "impurities" as well as their spatial distribution (zoning). One of the most important studies has been the examination of the hydrogen content of nominally anhydrous mantle phases. This includes (Mg,Fe)SiO₃ perovskite, which is believed to be the major phase of the lower mantle and is in fact the most abundant mineral in the planet. A key question is the extent to which hydrogen (in the form of OH or H₂O) is soluble in this mineral; if the solubility is high, the mineral may be a significant reservoir for water deep within the earth, an idea with major implications for the recycling of water within the planet, for evolution of the planet as a whole, and for its temperature distribution. Preliminary results obtained by C. Meade (Geophysical Laboratory) at U2B show that samples synthesized in large volume high-pressure devices can in fact contain a significant amount of hydrogen.

High Pressure (Diamond-Anvil Cell) Experiments; With the megabar diamond-anvil cell, it is now possible to produce static laboratory pressures in excess of those found at the center of the earth, i.e. greater than 3.6 million atmospheres (>360GPa). Since maximum pressure is achieved at the expense of sample size, experimen-

Figure 9 U2B: IR absorbance of a small (10µm) silicate sample showing a strong Si-O absorption band around 1000cm⁻¹. The width and shape of this band is consistent with the dominant silicate mineral being pyroxene ([Ca,Fe,Mg]SiO₃) rather than olivine ([Fe,Mg]₂SiO₄) or hydrated phyllosilicate. U. of Chicago and MVA, Inc. (Norcross, GA).

Figure 10 U2B: Microscopic IR absorption spectra of the intramolecular stretching vibrations (vibrons) of solid hydrogen at ultrahigh pressures and 85K temperature: (a) the low pressure phase, which exhibits a sharp peak beginning at 110 GPa indicative of a new phase transition, and a strong enhancement beginning at 150 GPa corresponding to the major phase transition; (b) the high pressure phase (up to 216 GPa), showing continued increase in intensity of the vibron which appeared at 150 GPa. The absorption measurements cover a spectral range of 3000-6500 cm^{-1} . Above 4800 cm^{-1} there are additional bands which can be assigned to combinations of vibrons with rotational excitations and lattice modes. M. Hanfland, R. J. Hemley, and H. K. Mao, Phys. Rev. Lett. **70**, 3760 (1993).

tation at such ultrahigh pressures depends on the ability to probe diminishingly small microscopic samples. For example, at pressures above 1 MBar ($>100\text{GPa}$), sample volumes are typically less than 10 picoliters. High-pressure optical spectroscopic methods used in conjunction with the diamond-anvil cell provide crucial, and often unique, information on the *in situ* physical and chemical properties of condensed matter.

The first IR absorption studies on hydrogen at ultrahigh pressures, a long standing problem in condensed-matter and planetary physics, have been carried out at U2B. A series of experiments has been performed on hydrogen to pressures of 216 GPa at temperatures of 77 - 295 K. In these experiments, measurements on hydrogen samples as small as $15\mu\text{m}$ in diameter by $1\mu\text{m}$

thick were obtained. A number of striking new features were observed that were not apparent in previous work carried out with conventional IR or laser spectroscopic techniques. The difference between the IR and Raman intramolecular stretching modes (vibrons) increases markedly with pressure, indicating a dramatic increase in intermolecular coupling. Studies were performed on a low-temperature phase transition at 150 GPa, which is associated with a discontinuous change in bonding properties in the molecular solid. These measurements showed a surprising and remarkable increase in absorption by over three orders of magnitude at the phase transition as well as the existence of an additional phase transition that was not evident in previous work (Figure 10). This extraordinary increase in absorption closely parallels the behavior of organic charge-transfer salts at ambient pressure, including pressure-induced neutral-to-ionic transitions. Preliminary work has been done on the new class of dense $\text{H}_2\text{O}-\text{H}_2$ clathrate compounds recently discovered by W. Vos, L. W. Finger, R. J. Hemley, and H. K. Mao, Phys. Rev. Lett. **71**, 3150 (1993).

Figure 11 U13UB: Real time visible light fluorescent image from a doped Yttrium Aluminum Garnet (YAG) type single crystal placed at the image plane of an Extreme UltraViolet Lithography (EUVL) camera. It shows line and space patterns: the $0.5\mu\text{m}$ and $0.375\mu\text{m}$ lines and spaces are clearly seen. The visible image is viewed with a microscope through the transparent single crystal phosphor. This optical arrangement results in spherical aberration and limits the spatial resolution that can be obtained with the existing microscope optics. Due to the high index of refraction of these phosphors, a spatial resolution down to $<0.1\mu\text{m}$ is expected, limited by the Rayleigh criterion of the visible fluorescence light. B. La Fontaine, O. R. Wood II, A. MacDowell, D. L. White, G. N. Taylor (AT&T Bell Labs).

SOFT X-RAY PROJECTION LITHOGRAPHY

A. MacDowell (AT&T Bell Laboratories) is exploring Extreme Ultraviolet Lithography (EUVL) as a possible new type of lithography for the beginning of the 21st century. It is a projection imaging technique that uses light of wavelength $\approx 130\text{\AA}$, provided by the U13U undulator, and an all mirror multilayer coated camera that can image features down to $0.1\mu\text{m}$ in size. Recent developments at U13UB include demonstration of sub-micron spatial imaging in real time using visible light fluorescence from a doped Yttrium Aluminum Garnet (YAG) type single crystal phosphor. Lines and spaces as small as $0.375\mu\text{m}$ have been clearly imaged (Figure 11). The spherical aberration of the visible light microscope provides the resolution limit at the present time; a spatial resolution less than $0.1\mu\text{m}$ (determined by the Rayleigh criterion of the visible fluorescence light) is expected owing to the high index of refraction of these phosphors. Such phosphors fluoresce when exposed to other photon wavelengths and could be used for real time sub-micron x-ray microscopy.

Acknowledgements

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NUCLEAR PHYSICS

Craig E. Thorn

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Special Interest Group Representative

I OVERVIEW

This year marked a significant broadening of the research effort at X5. User groups from Duke University, Universita di Roma, and University of Virginia completed three new experiments during the summer of 1993. In the fall, two groups, from Ohio State University and University of Virginia, began to set up and test detectors for experiments to be performed in the spring of 1994. The completion of the data analysis for earlier experiments was signaled by the submission and successful defense of four Ph.D. theses by students at Rensselaer Polytechnic Institute and Virginia Polytechnic Institute and State University. A Workshop on Photo-Reactions with Light Nuclei was held on September 13 and 14, 1993 to discuss recent data and calculations from BNL, Saskatoon, and Mainz. Finally, the major effort of the always-growing LEGS group, measurements of Compton scattering and pion photo-production on the proton, occupied the remainder of the beam time at X5, approximately 80 days.

II EQUIPMENT IMPROVEMENTS

The pion photo-production measurements require the tracking of protons and charged pions from the target to determine scattering angle, and to image the target cell to distinguish reactions originating in the mylar cell walls and the insulation from those coming from the cell contents. A set of eight multiwire proportional counters and associated readout electronics have been built for this purpose. These chambers produce position information that is much easier to interpret than do the existing drift chambers. They are now installed as part of two particle identification telescopes consisting of wire chambers, plastic scintillators and NaI(Tl) detectors.

A project to increase the gamma-ray beam energy to 406 MeV, begun last year, has been delayed by difficulties in obtaining funding. The heart of the

upgrade is a new frequency quadrupled ND-YLF laser that will produce approximately 5 watts of 260 nm light. At present, a prototype laser, constructed by STI Corporation, produces up to 7 watts of UV light, but the output power stability must be improved before it can produce a useful gamma-ray beam. We are presently preparing proposals for a SBIR grant and a CRADA to construct and test a stabilization scheme developed by our collaborators at INFN Frascati. This new laser will be mounted on the same granite optical bench as the existing AR-Ion laser, with its own computer controlled optical system, so that operation can quickly and easily be switched between the two lasers.

In order to decrease the time required to analyze the data from the increasingly complex experiments at LEGS, a DEC Alpha 3000/300 AXP computer was added to our VAX cluster. It will be used primarily for Monte-Carlo simulations to determine detector efficiencies. The LEGS data analysis cluster now consists of the Alpha AXP, two VAX Station 4000's, a VAX Station 3100 and a micro VAX II.

III PHOTO-REACTION WORKSHOP

A "Micro-Workshop", sponsored by the LEGS group, was held at Brookhaven on September 13-14, 1993. The occasion for this workshop was the completion of the deuteron photo-disintegration data analysis to produce final results for the cross section and asymmetry from 180 to 320 MeV obtained from Experiments L1, L3a, and L3b. The LEGS data, as well as recent data from Saskatoon and new calculations were discussed. Hartmuth Arenhoevel of Universität Mainz, who spent the summer at BNL, showed preliminary results of his new calculations. A paper describing these calculations and the new data is being prepared for publication in Physical Review.

Figure 1 X5: Experimental arrangement used to measure the $p(\gamma, \gamma p)$ and the $p(\gamma, \pi^0 p)$ reactions at 60° , 90° , and 120° for linearly polarized tagged gamma rays from 210 to 330 MeV. The channels are separated by detecting the photons in a high resolution NaI

spectrometer in coincidence with recoil protons whose trajectories are tracked through wire chambers and whose energies are measured by energy deposition and by time-of-flight in an array of plastic scintillators.

IV EXPERIMENT L8: E2 EXCITATION OF THE DELTA FROM COMPTON SCATTERING ON THE PROTON

In constituent quark models, a tensor interaction, mixing quark spins with their relative motion, is introduced to reproduce the observed baryon spectrum. A D state component is mixed into what would otherwise be a purely S wave object. This admixture breaks the spherical symmetry, creating a non-vanishing $\langle r^2 Y_{20} \rangle$ matrix element for the nucleon, and a deformation and static quadrupole moment for its first excited state, the delta resonance at ~ 325 MeV. The magnitude and sign of the D state component are quite sensitive to the internal structure of the proton, and have been a topic of great interest in recent years.

The intrinsic deformation of the spin 1/2 nucleon cannot be observed directly: it must be inferred from transition amplitudes, as in $N \rightarrow \Delta$. In a spherical bag model, the Δ is a pure quark-spin flip transition, which proceeds only through M1 excitation. If there are D state admixtures in the nucleon or Δ , then quadrupole excitation is also allowed. A variety of models predict the mixing

of the E2 with the dominant M1 to be quite small, from -0.9% to -6%, so that a high degree of precision is demanded of an experiment. The E2 component has never been definitively observed. Compton (elastic) scattering of polarized photons is a unique tool for enhancing the signal of an E2 component, because the polarization degree of freedom can be used to directly cancel the contribution of almost all background amplitudes, substantially reducing the dependence on a reaction model. As part of a larger program to determine the E2 amplitude, we have measured the $p(\gamma, \gamma p)$ reaction at 60° , 90° and 120° for linearly polarized tagged gamma-rays from 210 to 330 MeV. The principal experimental background comes from the $p(\gamma, \pi^0 p)$ reaction, where one of the high energy photons from π^0 decay is detected. The cross section for this process is about 200 times that for Compton scattering. In this experiment, these channels were separated by detecting the photons in a high resolution NaI spectrometer in coincidence with recoil protons whose trajectories were tracked through wire chambers and whose energies were measured by energy deposition and by time-of-flight (TOF) in an array of plastic scintillators. This arrangement is shown in Figure 1. The π^0 decay photons closest in energy to Compton scattering are accompanied by low energy photons traveling in

nearly the opposite direction. These were suppressed by additional NaI veto detectors placed opposite the high energy γ -ray spectrometer.

A typical γ/π^0 separation is shown in Figure 2, where the γ -ray energy is plotted against proton TOF. The energy and TOF expected for Compton scattering, as calculated from the tagged beam energy and the measured proton recoil angle, have been subtracted. Compton scattering is cleanly separated from the much larger pion photo-production.

Preliminary results for the 90° (center of mass) photon beam asymmetry are shown in Figure 3 (solid circles). Also shown in Figure 3 is the only published datum for this observable (open diamond). If only M1 scattering contributed, the asymmetry would have the value $3/7$, independent of energy. The fact that this is not true indicates the importance of other multipoles, especially off the resonance energy. Measurements of the beam asymmetry made at the other two scattering angles and measurements yet to be made for other polarization observables will be used to isolate the contribution of the resonant E2 amplitude.

The difficulty of using models to extract the small E2 amplitude from the data is indicated by the variety of

predictions produced by the different models currently available. The only calculation in reasonable agreement with the beam asymmetry at this angle (the solid curve in Figure 3) predicts an unpolarized cross section significantly higher than the measured values.

V EXP. L14 AND L16: DELTA PROPAGATION IN NUCLEI FROM $^{16}\text{O}(\gamma,\gamma)$ AND $^4\text{He}(\gamma,\gamma)$

User groups from Universita di Roma and University of Virginia have used a slightly modified arrangement of the proton Compton scattering experiment to observe Compton scattering of linearly polarized photons from ^{16}O and ^4He . These experiments are designed to investigate the behavior of the delta resonance in the nuclear medium. Calculations using a delta-hole model show that the beam asymmetry is very sensitive to these medium effects. Although similar information can be obtained from pion-nucleus scattering, the photon is a more nearly ideal probe, since there is almost no attenuation or distortion in the incoming and outgoing channels, and the photon samples the entire nuclear volume. These experiments have just been completed, and the data is now being analyzed to produce cross sections and asymmetries as a function of scattering angle and incident energy.

VI EXPT. L15: D STATE COMPONENT IN THE ${}^4\text{He}$ NUCLEAR WAVEFUNCTION FROM ${}^4\text{He}(\gamma, \text{DD})$

The beam asymmetry for the photo-disintegration of ${}^4\text{He}$ into two deuterons provides a clean measure of a D state component in the predominantly spherically symmetric ${}^4\text{He}$ wavefunction. The tensor component of the nuclear force creates the D state admixture, in an analogous way to the creation of the D state in the nucleon by the tensor component of the quark interaction. This experiment was performed by a group from Duke University, in parallel with the Compton scattering on ${}^4\text{He}$, but using a different set of detectors for the deuterons. The data is presently being analyzed to extract asymmetries.

TIME RESOLVED SPECTROSCOPY

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Special Interest Group Representative

I INTRODUCTION

Since the inception of 2nd generation synchrotrons, the possibility of using the pulsed nature of the light for time resolved experiments has been presented as a selling point. At the NSLS, a number of groups have turned this promise into reality. A wide variety of time-resolved experiments, employing both the VUV and X-Ray Rings to supply wavelengths from the far infrared to the hard X-Ray regions, are presently carried out on gases, liquids, solids, and surfaces. The time domain ranges from subnanosecond to the synchrotron interpulse period, which, along with other ring parameters relevant to pulsed time-resolved investigations, are given in Table I.

The majority of pulsed, time-resolved studies require special single-bunch operations. This is so because a long time window between synchrotron pulses is required in some experiments if slow decays are to be recorded; in others, a long time window prevents the overlap of the photoion time-of-flight spectra initiated by each synchrotron pulse. In addition, the number of photons per pulse is increased in single-bunch operations, by factors of ~ 3 on the VUV Ring and ~ 10 on the X-Ray Ring. This is advantageous for experiments which have duty-factor limitations imposed by detectors or by pump-sources in pump-probe studies and also for a new

photon-correlation experiment in progress at X1B. Presently, the X-Ray Ring is formally scheduled for approximately 6 days of single-bunch operations per scheduling trimester. Five-bunch operations, because it has less impact on ordinary users, is also scheduled but can be profitably used by fewer timing groups. In general, timing operations on the VUV Ring are scheduled with less formality. Timing shifts, for single bunch or special operation of the 4th harmonic cavity described below, are provided based on requests made during the weekly users' meeting. Shifts available for request are the midnight-to-8 am shifts everyday and Saturday, Sunday and Monday evenings beginning at 6 pm. In addition, a week of timing operations is occasionally formally allocated on the long range schedule.

II X-RAY RING

In last year's annual report, time-resolved investigations on the X-Ray Ring were highlighted. Therefore only a brief enumeration of the programs will be included here, after which investigations performed on the VUV Ring are emphasized. In the past year, at least eight groups mounted experiments requiring single-bunch operations on the X-Ray Ring. Three beam lines, X1B, X6, and X12 were involved in single-bunch timing experiments for the first time.

Table I. Storage-ring characteristics relevant to time-resolved experiments.

	RF frequency	Maximum number of bunches	Minimum interpulse period	Maximum interpulse period (single bunch)	Nominal pulse duration (FWHM)
VUV Ring	53 MHz	9	19 ns	170 ns	1.5 ns (a)
X-Ray Ring	53 MHz	30	19 ns	566 ns	.6 ns (b)

(a) With 4th harmonic cavity powered, trapezoidal profile as seen in Figure 3. Pulse lengths of 200 ps may be available in the future in special operations.

(b) Single bunch.

Figure 1 X25: Time evolution of the nuclear forward scattering from ^{57}Fe nuclei in a thin Fe film after they have been resonantly excited by a 14.4-keV synchrotron pulse. The gamma rays emitted by the nuclei possess slightly different energies, which depend on the splittings of the nuclear magnetic sublevels in the internal magnetic field, H_{int} , of the ferromagnetic film. The coherent addition of the different energies leads to beats, as seen, from which H_{int} is measured. As the temperature of the

film is raised through the Curie point at 1043 K, the beats disappear, along with H_{int} . In addition, the temperature dependence of the mean square displacement of the nuclei can be estimated from the envelope of the time evolution through analysis of the Lamb-Mössbauer factor, analogous to the familiar Debye-Waller factor. U. Bergmann (SUNY-Stony Brook) and S. Shastri (Cornell U).

Ian McNulty and co-workers began testing detectors to be used in a new x-ray rendition of the classic Hanbury-Brown-Twiss experiment. The experiment will characterize the transverse coherence of low emittance sources (beginning with the X1 undulator) by cross-correlating photon intensity fluctuations at different points along the vertical dimension of the x-ray beam. Single-bunch operations are required since the number of coincidences measured between two points depends on the square of the number of photons per pulse (see abstract under X1B in this volume).

Two groups, Tom Lebrun (ANL) and co-workers and Jon Levin (U. Tennessee) and co-workers, studied photoionization processes in inert gases. They used photoion time-of-flight techniques to separate the host of multiply charged photoion species which ensues in the vacancy cascade following K-shell photoionization.

Nuclear resonant scattering experiments were pursued by three groups: U. Bergmann (SUNY-Stony Brook)

and co-workers, Gilbert Hoy (Old Dominion U.) and co-workers, and Ercan Alp (ANL) and co-workers. These experiments record the time-dependent emission of gamma rays from nuclei which have been resonantly excited with a hard x-ray pulse. The narrow widths of nuclear levels means that the emission decays over hundreds of nanoseconds, requiring single-bunch operations in order to record the information contained in the decay profile (see Figure 1 and abstracts under X25 in this volume).

By measuring excited-state fluorescence, Jack Preses, Dick Holroyd (BNL) and co-workers examined the yield of excited states generated along the tracks of photoelectrons which are ejected by x-ray absorption events in hydrocarbon liquids. The dependence of the excited state yield on x-ray energy is of fundamental interest to radiation chemistry. In addition, they began a study of x-ray excited luminescence in porous silicon (see abstract under X7B, this volume).

Bruce Itchkawitz (Fritz-Haber Inst., Berlin), Jim Long (NRL) and co-workers applied photoelectron spec-

troscopy to examine the energy distribution, time-decay, and pump-intensity dependence of laser-excited electron states in thin films of the fullerene C_{60} . This work requires single-bunch operations because of the low repetition-rate pulsed-laser used to pump the samples (see abstract under X24C, this volume).

III VUV RING

An important issue for pulsed, time-resolved, experiments on the VUV Ring concerns the recent installation of a powered 4th-harmonic radio frequency (RF) cavity. The cavity was developed to increase the beam lifetime. It works by increasing the length of the circulating electron bunch, thereby reducing the bunch's electron concentration and with it, the electron-electron scattering losses (Touschek scattering). For some time-resolved experiments there is an added dividend because, when actively powered, the cavity effectively fixes the mean pulse length throughout a fill; otherwise the pulse length decreases as the beam current decays, a general characteristic of storage rings. Thus time-resolved experiments which rely on deconvolution to remove the synchrotron pulse shape from decay data will benefit from the constant pulse profile, provided that the amount of pulse stretching is not too severe. Experiments performed on U9B have shown that for synchrotron-excited fluorescent-decay data, where accurate measurements of the synchrotron pulse-profile are possible, the constancy in pulse shape outweighs the disadvantage of working with longer synchrotron pulses.

The powered 4th harmonic cavity can also be phased to *decrease* the pulse duration. Calculations indicate that pulses less than 200 ps FWHM are feasible. The resultant decrease in lifetime will necessitate that the short-pulse mode be relegated to special operations. In the future it is likely that the cavity will be used in a short-pulse mode for experiments where it is not convenient to measure the pulse profile accurately or where the shortest possible excitation is desired to extract rapid decays.

U4IR, U2B

Using beamlines U4IR and U2B, Larry Carr (Grumman) and co-workers have been applying mid- and far-infrared (IR) radiation (2-100 μm) to study the dynamics of electronic excitations in semiconductors and superconductors. These materials are amenable to study with pump-probe techniques, wherein the sample is pumped by a laser pulse (to create electron-hole pairs in a semiconductor and quasi-particles in a superconductor) and subsequently probed with an IR pulse, which detects changes in the absorption spectrum caused by the presence of the nonequilibrium carriers. Special, single-bunch

operations are usually used in these investigations in order to increase the time window between synchrotron pulses. Before the development of infrared beam lines, these experiments were not feasible because continuously tunable, pulsed sources of mid- and far-infrared radiation (2-100 μm) were unavailable. While laser techniques can provide pulses in a similar wavelength range, broadly continuous tuning is not possible and, for wavelengths beyond 10 μm , pulse durations less than 10 ns are extremely difficult to achieve and the pulse repetition rate is low.

In addition to the pump-probe technique, a second type of new experiment has been developed where the IR pulses themselves serve as the photoexcitation source and the induced transient photoconductivity is measured electrically, for example with a sampling scope. These experiments benefit from single-bunch operations because of the increased time window and because the number of photons per pulse, and therefore the instantaneous signal, is about 3 times greater than in ordinary 7

Figure 2 U4IR: Nanosecond, time-resolved, far-infrared transmission spectra showing the increased transmission induced in a superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ film at 80 K by a 100 ps, 532 nm laser pulse. The listed times give the delay between the arrival of the laser pulse and the later synchrotron pulse. The solid curve shows the transmission change caused by a 3 K static temperature rise. Note the similarity of the laser-induced change in the far-IR absorption spectrum to temperature-induced change, suggesting a thermal mechanism for the response on this time scale. G.L. Carr (Grumman), D.B. Romero and D.B. Tanner (U. Florida), S. Etemad and A. Inam (Bellcore), W. O'Brien (U. Tennessee), D. Ederer (then at NIST), C.J. Hirschmugl and G.P. Williams (NSLS).

bunch fills. Two recent examples of IR-excited photoconductivity, one on GaAs/Al_xGa_{1-x}As quantum well IR detectors and a second on Hg_{1-x}Cd_xTe thin films, are described in the abstracts under U4IR in this volume.

A transient population of quasi-particles is created in a superconductor when pairs in the superconducting condensate are broken by the absorption of a laser pulse. Knowledge of the energy distribution and the decay of the quasi-particle population is important to theories of non-equilibrium superconductivity. These quantities are accessible to far-IR absorption spectroscopy because the quasi-particle population modifies the IR absorption spectrum. The first experiment of this sort involved a collaboration of Grumman, Bellcore, NSLS, and U. Florida. Thin films of the high- T_c superconductor YBCO, held at 80 K, were pumped with ~100-ps, 532-nm pulses from a Nd:YAG laser whose pulse train was locked to the VUV Ring. The IR absorption spectrum was measured using synchrotron pulses controllably delayed after the laser pump-pulse, as shown in Figure 2. It was found that an ordinary thermal mechanism was responsible for the response of YBCO beyond a nanosecond. However, more recent studies have uncovered a smaller, faster (<1 ns) response component with an enhanced response for photon energies approaching $4k_B T_c$, the average pair condensation energy in BCS theory, which suggests a pair-breaking (non-thermal) mechanism may also be operating, but on a faster time scale.

Similar far-IR pump-probe experiments have also been carried out on the semiconductor Hg_{1-x}Cd_xTe, an important small bandgap material used in IR detectors. In a semiconductor, pump-induced changes in the far-IR transmission spectrum originate from the population of free electron-hole pairs generated by the laser pulse. This population absorbs IR directly through intraband transitions (free-carrier absorption). A time-resolved measurement of the far-IR absorption spectrum permits a unique and richly detailed understanding of the transport properties of the very carriers important to the operation of photodetector devices. For example, a wavelength-dependent measurement of the absorptive losses amounts to a measurement of the frequency-dependent electrical conductivity, from which the momentum scattering time of the excited carriers can be inferred. Furthermore, the absolute laser-excited carrier density can be quantified, and bulk and surface recombination rates estimated.

Separate measurement of all these parameters is not possible with ordinary transport measurements.

U9B

Techniques for measuring time-, wavelength-, and polarization-resolved fluorescence have been developed by John Sutherland and co-workers on U9B and applied primarily to biological problems. These investigations seek to determine structural and motional properties of proteins in their natural aqueous environments where most classical structural probes, such as diffraction, are inapplicable. The experiments capitalize on the widespread biological distribution of three fluorescent amino acids, tryptophan, tyrosine, and phenylalanine, each with absorption bands in the UV below the water-cutoff of about 7 eV. Amino acids are building blocks of peptides, which are themselves structural units of proteins. Static structural information of peptides containing the fluorescent amino acids may be encoded in the detailed time decay of their fluorescence after pulsed excitation by

Figure 3 U9B: Fluorescence decay of Ala(16)-gramicidin, a peptide which is found in bilayer membranes and which contains tryptophan, an amino acid which fluoresces when excited by a pulse of synchrotron radiation. The synchrotron pulse is also pictured, seen with the trapezoidal profile imposed by the active 4th harmonic cavity installed on the VUV Ring. The fluorescence lifetime measurement was part of a characterization which also included measurements of circular dichroism and fluorescence anisotropy, which is a measure of the fluorescence depolarization sensitive to peptide motion as described in the text. S. Scarlata, J. Elliot, L. Clipp (SUNY-Stony Brook), K. Polewski and J. Trunk (BNL).

Figure 4 U9B: Time decay of the luminescence from the Ce^{3+} dopant in the scintillator $\text{Gd}_2(\text{SiO}_3)_2\text{O}:\text{Ce}$ after gamma-ray and selective UV excitation. When excited with gamma rays, the blue (420 nm) luminescence decays with the complicated profile seen in the left panel. The decay clearly cannot be understood as a direct transfer of energy from the gamma-generated electron-hole pairs to the Ce^{3+} center, which, when excited directly, decays more simply, as pictured. In the right panel, it is seen that the gamma-excited

luminescence decay-profile corresponds to a superposition of the two profiles ensuing after separate, direct UV-excitation of two Gd^{3+} excited states, $^6\text{I}_7$ (at 275 nm) and $^6\text{P}_7$ (at 313 nm). This suggests that gamma-excitation of the Ce^{3+} luminescent center proceeds predominantly through excitation of Gd^{3+} , which then resonantly transfers energy to the Ce^{3+} center. H. Suzuki, T.A. Tombrello (Caltech), C.L. Melcher and J.S. Schweitzer (Schlumberger-Doll).

synchrotron radiation. For example, the presence of inequivalent conformations in a sample are frequently not revealed by either absorption or emission spectra, but may be revealed by multiple fluorescent lifetimes. By including polarization detection, dynamical structural information can be extracted, e.g. the time scale for rotational or nutational motion. This is possible because such motion alters the polarization of the fluorescence, converting it from its initially excited direction parallel to the synchrotron radiation to the perpendicular direction. Thus, peptide motion, if it occurs during the fluorescent lifetime, will be revealed by a decay of the parallel (perpendicular) component faster (slower) than the polarization-integrated lifetime (Figure 3). The polarization behavior is usually summarized by the “fluorescence anisotropy”, which is the (time-dependent) normalized difference between parallel and perpendicular intensities.

Since the decay time of the synchrotron-excited fluorescence in biological specimens seldom exceeds ~ 4 ns, less than the interpulse period of 19 ns of ordinary 7 bunch fills, single bunch operations are not required. However, the short fluorescent decay times require accurate knowledge of the synchrotron pulse profile. The time-correlated single-photon counting techniques employed in the fluorimeter permit a measurement of both the fluores-

cence decay and the exciting synchrotron pulse, as seen in Figure 3, with 100 ps resolution. Clearly, a stable synchrotron pulse length is essential to these experiments, which have benefited from the improved pulse-length stability established by the recently commissioned active 4th-harmonic cavity described above.

While laser-based sources can also provide short pulses over much of the biologically relevant photon energy range for which U9B is optimized, the required optical-mixing techniques make tuning over a wide range extremely cumbersome. An interesting use of the nimble tuning provided by synchrotron radiation occurs in an experiment undertaken by Jeff Schweitzer and co-workers, who have elucidated the scintillation mechanism of the inorganic scintillator $\text{Gd}_2(\text{SO}_4)_2\text{O}:\text{Ce}$ (GSO), which has application as a gamma ray detector. Tunable UV, within the range of U9B, permits selective excitation of different excited states in the material. The rate of energy transfer from each excited state to the luminescent center, on the Ce^{3+} dopant, can be monitored by recording the time-response of the Ce^{3+} luminescence at 420 nm after the selective excitation, as explained in Figure 4 (see also the abstract under U9B in this volume). The long time decays of the luminescence required the use of single-bunch shifts.

UV PHOTOEMISSION AND SURFACE SCIENCE

Chi-Chang Kao

NSLS

VALENCE BAND PHOTOEMISSION

High resolution valence band photoemission, resonant photoemission, and soft x-ray absorption were used to study the metal-insulator transition of V_2O_3 at beamline U4B by J.H. Park, L.H. Tjeng, J.W. Allen (U. of Michigan), P. Metcalf (Purdue University), and C.T. Chen (AT&T Bell Labs). Gap opening in the insulating phase was clearly observed in the valence band photoemission spectra shown in Figure 1.

From these spectroscopic data, the authors suggest that the O 2p to V 3d charge transfer energy is much smaller than the value expected previously, and that the hybridization between the V 3d and O 2p should be treated explicitly. The addition of a new physical parameter (the hybridization term) included in this approach may lead to a better understanding of the complicated pressure and composition dependence of the metal-insulator transitions in these materials.

Figure 1 U4B: High resolution valence band photoemission spectra of an annealed stoichiometric single crystal of V_2O_3 above ($T=170K$, dotted line) and below ($T=130K$, solid line) the metal-insulator transition temperature ($T_t=155K$). The photon energy is 110 eV. Gap opening in the insulating phase is clearly observed, implying that the O 2p to V 3d charge transfer energy is much smaller than expected and that the hybridization between the V 3d and O 2p should be treated explicitly. J.-H. Park, L. H. Tjeng, J. W. Allen (U. Michigan), P. Metcalf (Purdue U.), and C. T. Chen (AT&T Bell Labs).

CORE LEVEL PHOTOEMISSION

High resolution core-level photoemission continued to be the workhorse in the study of a wide variety of systems, ranging from surface reconstruction of clean (U16A) and adsorbed surfaces (U12B, U3C), to surface segregation (U12B), interfacial bonding in bi-metallic materials (U16A), and surface chemical reactions (U16B, U8B).

One example of high resolution core-level photoemission was a study of the adsorption, desorption, and decomposition mechanisms of a series of isostructural molecules (PH_3 , PF_3 , and PCl_3) on the Ru(0001) surface at beamline U3C by H.-S. Tao, U. Diebold, T.E. Madey (Rutgers U.) and N.D. Shinn (Sandia National Lab). Large chemical shifts in the P 2p binding energy for the individual PX_n species, where $X = H, F, Cl$ and n ranges from 0 to 3, allow quantitative identification of the surface intermediates as a function of surface temperature and initial reactant exposure.

Figure 2 shows some representative spectra: curve (a) shows the spin-orbit split P 2p core level of PF_3 molecularly adsorbed on Ru(0001) at 150K, and curve (b) shows the P 2p of the same system after photon or electron induced defluorination. Well-resolved peaks are observed for PF_3 , PF, and P surface species. In contrast, both PCl_3 and PH_3 adsorb dissociatively on Ru(0001) at 150K, as shown in curves (c) and (d).

The effort towards the development of a novel dielectric thin film deposition technique using UV and soft x-ray induced reaction continues at beamline U7A by J.F. Moore, D.R. Strongin (SUNY-Stony Brook), M. Strongin, and M.W. Ruckman (BNL Physics). The technique involves condensing a reactive mixture of gases onto a substrate at low temperature, and subsequently exposing the reactants to white radiation in order to convert them into a dielectric film. The unreacted materials or volatile products are then desorbed by warming the substrate to ambient temperature.

SPIN-POLARIZED PHOTOEMISSION

Two new spin-polarized photoemission experimental stations were commissioned recently to exploit the high photon flux available in the soft x-ray regime at beamlines U13UA and X1B. These new experimental stations, combined with the high resolution spherical grating monochromators, make it possible to study the deeper core levels of 3d transition metals and their compounds.

Figure 2 U3C: Representative high resolution core-level photoemission spectra for a series of isostructural molecules (PH_3 , PF_3 , and PCl_3) adsorbed on the Ru(0001) surface at 150K. (a) The single spin-orbit split peak at 133.4eV binding energy ($\text{P } 2p_{3/2}$) is indicative of PF_3 adsorption. (b) Electron and photon irradiation induces sequential defluorination (discrete peaks are observed for each of the PF_2 , PF and P surface species). (c) and (d) In contrast, both PH_3 and PCl_3 adsorb dissociatively at 150K: for PH_3 , both atomic P and an unspecified PH_x moiety co-exist with the parent PH_3 molecule, and for PCl_3 , the major dissociation intermediate is PCl . H.-S. Tao, U. Diebold, T.E. Madey (Rutgers U.) and N.D. Shinn (Sandia National Lab).

Figure 3 U13UA: Spin-resolved Fe 2p photoemission spectra from a 20 ML thick Fe film epitaxially grown on a Ag(001) substrate, using soft x-ray photons ($h\nu=760\text{eV}$) linearly polarized in the direction of sample magnetization. Both spin-orbit split components ($2p_{3/2}$ and $2p_{1/2}$) are shown. The full lines show best fits of Doniach-Sunjić lineshapes to the spin-majority and spin-minority spectra. The Fe $2p_{3/2}$ component exhibits an exchange splitting of $0.42 \pm 0.05\text{eV}$ which is close to the splitting found in Fe 3p photoemission (0.45 eV) as well as in Fe 2p core level magnetic circular dichroism (MCD), suggesting similar origin for these effects. The exchange splitting of the $1/2$ component is of the same magnitude (within experimental uncertainty) and the same sign (majority having lower binding energy) as the $3/2$ component. However, the polarization of the $3/2$ and $1/2$ components is of opposite sign, as expected in a simple atomic picture owing to the different spin population of the $3/2$ and $1/2$ components. B. Sinkovic and E. Shekel (NYU).

One experimental station was designed and constructed by Boris Sinkovic and his group at NYU. The electron energy, angle and spin-resolving spectrometer combines a large hemispherical analyzer (VSW HA100) and home-built version of the low-energy (NIST type) spin detector. The electron spectrometer with its large ($2 \times 10\text{mm}$) focal point well matches the U13UA photon beam profile.

The first series of experiments by the Sinkovic group were performed on a 20 ML thick Fe film epitaxially grown on a Ag(001) substrate. The saturation magnetization fields were determined via *in situ* measurement of the magneto-optical Kerr rotation. The spin polarized photoemission data were taken using 760eV soft x-ray photons linearly polarized in the direction of sample magnetization. The spin-resolved spectra of the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ spin-orbit split components are shown in Figure 3. The full lines show best fits of Doniach-Sunjić lineshapes to the spin-majority and spin-

Figure 4 X1B: Spin-polarized Cr 3p core level soft x-ray ($h\nu=250\text{eV}$) photoemission spectra from 1 Å of Cr on Fe(100) at room temperature. Open triangles: minority spin, solid triangles: majority spin. The large exchange splitting exhibited in the 3p core level provides the first direct evidence of an enhanced magnetic moment for this system. With subsequent deposition, each new layer of Cr couples antiferromagnetically to its neighbor and as the Cr film thickens, the average magnetic moment on the Cr sites slowly reduces to that characteristic of bulk Cr. J. Xu, P. D. Johnson (BNL Physics) and B. Itchkawitz (Fritz-Haber Institute).

minority spectra. The Fe $2p_{3/2}$ component exhibits an exchange splitting of $0.42 \pm 0.05\text{eV}$ which is close to the splitting found in Fe 3p photoemission (0.45 eV) as well as in Fe 2p core level magnetic circular dichroism (MCD), suggesting similar origin for these effects. The exchange splitting of the $1/2$ component is of the same magnitude (within experimental uncertainty) and the same sign (majority having lower binding energy) as the $3/2$ component. However, the polarization of $3/2$ and $1/2$ components have opposite sign, as expected in a simple atomic picture owing to the different spin population of $3/2$ and $1/2$ components.

The second spin-polarized experimental station was designed and constructed by J. Xu and P.D. Johnson (BNL Physics). As an example of their first results, a spin-polarized photoemission study of Cr on Fe(001) at beamline X1B by J. Xu, P. D. Johnson (BNL Physics) and B. Itchkawitz (Fritz-Haber Institute) will be summarized here. Several theories have predicted that a monolayer of chromium deposited on an Fe(001) surface will be antiferromagnetically coupled to the substrate with an enhanced magnetic moment of the order of 3.0 Bohr magnetons. By examining the spin polarization of the Cr 3p core level for submonolayer Cr coverages, the experiment confirmed both the theoretical predictions and earlier experimental studies in showing that the moments

on the chromium atoms are indeed aligned antiparallel to the substrate moments. As shown in Figure 4, the large exchange splitting observed in the 3p core level also provided the first direct evidence of the enhanced magnetic moment. With subsequent deposition, the studies were able to show that each new layer of Cr couples antiferromagnetically to its neighbor and that as the Cr film thickens, the average magnetic moment on the Cr sites slowly reduces to that characteristic of bulk Cr.

FAR INFRARED SPECTROSCOPY

FY93 saw a dramatic increase in the use of far-infrared radiation from the U4IR beamline for *in situ* studies of electrode/electrolyte interfaces. For example, the adsorption of perchlorate and chloride ions on Ag(111) was reported by A.E. Russell (U. of Liverpool), G.P. Williams (NSLS), A.S. Lin (George Washington U.), and W.E. O'Grady (NRL). The coupling efficiency between source and sample at U4IR is found to be three orders of magnitude greater than that of a 2000K black body source. Figure 5 shows the Ag-Cl stretching vibration observed for a single crystal Ag(111) electrode in 0.1 mol dm^{-3} HClO_4 solution. The band centered at 190 cm^{-1} is attributed to the formation of adsorbed chloride from the slow reduction of perchloride.

Figure 5 U4IR: Far Infrared *in situ* study of an electrochemical interface: Ag-Cl stretching vibration observed for a single crystal Ag(111) electrode in 0.1 mol dm^{-3} HClO_4 solution. The band centered at 190 cm^{-1} is attributed to the formation of adsorbed chloride from the slow reduction of perchloride. The coupling efficiency between source and sample at U4IR is found to be three orders of magnitude greater than that of a 2000K black body source. A.E. Russell (U. of Liverpool), G.P. Williams (NSLS), A.S. Lin (George Washington U.) and W.E. O'Grady (NRL).

X-RAY ABSORPTION SPECTROSCOPY

Lars Furenlid
NSLS

1993 was a stellar year for x-ray absorption spectroscopy at the NSLS, with increases in the experimental capabilities of individual beamlines, the level of support provided by the facility, and, more importantly, in the number of publications and abstracts reported by the user community. Six beamlines at the NSLS are dedicated to x-ray absorption spectroscopy (XAS), with a further five or six beamlines spending at least part of the time in a spectroscopy mode. An estimated 500 researchers and collaborators from 101 universities, 24 corporations and 7 national laboratories and representing 46 nations are currently pursuing research with x-ray absorption spectroscopy at the NSLS.

The extended x-ray absorption fine structure (EXAFS) technique is the tool of choice for determining structural aspects of near-neighbor interactions in sample systems lacking long-range order such as solutions, clusters, amorphous powders, heterogeneous mixtures, and thin films. X-ray absorption near-edge spectroscopy (XANES) provides complementary information about oxidation states and geometries. The sample can be solid, liquid, or even gaseous; at any temperature; at any pressure; and subject to any variety of conditions limited only by the experimenters' ingenuity. This versatility has resulted in the application of XAS to a vast range of problems. The diversity of sciences making use of XANES and EXAFS techniques is well represented in the more than 150 abstracts from beamlines X6B, X9B, X10C, X11A, X15B, X18B, X19A, X23A2, and X23B found in the latter parts of this Report. Soft x-ray absorption spectroscopy is performed at and represented in the abstracts of beamlines X1B, U1A, U4B, and U16B.

STRUCTURAL BIOLOGY

XAS is an effective tool for studying metal binding sites in biological molecules and there were many important experiments in the last year, a few of which are highlighted here:

L. Chen, D. Tiede, P. Montano, and J. Norris (ANL), Z. Wang (U. of Chicago), and H. Scheer (U. of Munich) studied chemically modified bacterial photosynthetic reaction centers at beamline X6B. By substitut-

ing Ni and Zn for Mg in the natural molecular system used by certain bacteria to harness solar energy, the researchers can study the structural changes occurring during the initial electron transfer step. EXAFS and XANES studies of Ni-containing reaction centers were compared with isolated model complexes, and it was found that the normally 4-coordinate Ni becomes 5- or 6-coordinate in the reaction center as the temperature is reduced to 20K (Figure 1). In further experiments on beamline X23A2, this group probed the temperature dependence of the environment around the Fe atom in the reaction center which participates as part of the electron transfer chain. Preliminary results suggest that the structure does change upon cooling from room temperature to 20K.

L. Que Jr., C. Randall, A. True and R. Holz (U. of Minnesota) and R. Scarow (Haverford College) studied the structure around both iron atoms in the mixed-valent active form of uteroferrin at beamline X9B [see *J. Am. Chem. Soc.* **115**, 4246 (1993)]. They propose the presence of a hydroxo- or alkoxo- bridged di-iron unit. The

Figure 1 X6B: XANES spectra of Ni-substituted bacterial photosynthetic reaction center and isolated Ni bacteriochlorophyll A at 20K. L. Chen, D. Tiede, P. Montano, and J. Norris (ANL), Z. Wang (U. of Chicago) and H. Scheer (U. of Munich).

Fe(III) site is suggested to have tyrosine and histidine as further ligands, whereas the Fe(II) site has histidine and a chelated carboxylate.

K. Zhang and J. Dong (Biostructures Institute) and R. Korszun (BNL Biology) performed polarized EXAFS studies on myoglobin single crystals at beamline X9A. Making use of the plane polarization of the x-ray beam and appropriately orienting a crystal with a goniometer, they were able to separately measure the Fe K-edge EXAFS oscillations arising from neighboring atoms in and out of the plane of the heme group (a ring structure around the central iron atom). The four nitrogens of the heme are located at 2.03 Å from the Fe atom, whereas the axial ligands are at an average distance of 2.12 Å (Figure 2).

J. Wu, Y. Lu, E. Scheuring, L. Miller, A. Xie and M. Chance (Albert Einstein College of Medicine) and T. Nash (National Institutes of Health) studied whole cells of *Giardia lamblia*, a parasite of humans and other mammals, on beamline X9B. X-ray studies determined that *Giardia* contains large quantities of zinc. EXAFS experiments at the Zn K edge revealed that the data was adequately described as resulting from coordination by 4 S and 0.5 N. This is consistent with the zinc binding to cysteines and histidines (or water) as would be expected for large quantities of zinc-finger proteins.

ENVIRONMENTAL SCIENCES

Researchers in the environmental sciences have started making heavy use of synchrotron techniques for the characterization of soil and mineral samples, exploit-

Figure 2 X9A: Polarized EXAFS oscillations of met-myoglobin with the x-ray polarization parallel (solid) and perpendicular (dashed) to the heme plane. K. Zhang, J. Dong (Biostructures Institute) and R. Korszun (BNL Biology).

Figure 3 X11A: Isolated Pb L₃-edge spectra of (a) lead sulfide, (b) contaminated soil incubated with a sulfide source, (c) tetraethyl lead, and (d) soil contaminated with organic leads. (b) also shows a soil sample sulfide-treated and stabilized with cement (dashed). M. Kelley (DuPont) and G. Lamble (NSLS).

ing the elemental specificity and sensitivity of XAS techniques. The principal areas of research center around the identification and quantitation of the chemical forms of heavy metals in samples and the evaluation of the efficacy of various remediation strategies.

M. Kelley (DuPont) and G. Lamble (NSLS) continued their studies of remediation strategies for heavy metals in the environment. By utilizing the EXAFS oscillations as fingerprints, they were able to monitor the effectiveness of sulfiding soils containing alkyl leads - the relatively volatile complexes used in the past by the petroleum industry to increase the octane rating of gasolines. In spectra measured at beamline X11A, the lead in contaminated soil containing "motor mix" could be seen to change chemical state after incubation with a sulfide source. Efforts to physically stabilize the sample with cement resulted in further spectral changes, which appear consistent with conversion from organic to inorganic lead (Figure 3). Together with S. Fendorf, D. Sparks and M. Stapleton (U. of Delaware), the researchers also studied the properties of chromium sorbed on silica. From consideration of quantitative EXAFS results at various surface coverages, it was concluded that the sorbed Cr(III) occurred as α -CrOOH phase. Environmental concerns about Cr(III) toxicity and mobility must thus consider the properties of this hydroxide phase.

R. Chianelli, A. Klaus and R. Prince (Exxon), G. George (SSRL), and I. Raskin (Rutgers U.) report plans to study phytoremediation: the potential exploitation of the sequestering of metal contaminants by plants. In proposed XAS experiments on beamline X10C, the experimenters will track the initiation and growth of inorganic phases of Pb and Cd in plants with periodic sampling.

C. Dodge and A. Francis (BNL Applied Science) and F. Lu (U. of Kentucky) performed XANES studies on photochemically-degraded uranyl citrate complexes. The researchers have developed a process for the recovery of uranium from contaminated soils, sludges and wastes via extraction with citric acid to form a uranium citrate complex. The uranium can then be precipitated from solution via photo degradation. From XANES studies performed on beamline X19A, the researchers have demonstrated that the uranium starts as U(VI) in the environment, is reduced to U(IV), and then reoxidized to U(VI).

A. Vairavamurthy, W. Zhou, and B. Manowitz of the Environmental Chemistry group at BNL studied environmental samples from sediments at Shelter Island. The researchers used XANES techniques on X19A to identify all the major forms of sulfur present in samples taken at varying depths. They discovered, for the first time, that a large fraction was in the form of sulfonic acids in all samples. Research continues to determine the

geochemical role of these complexes. The group also studied the ramifications of using hydrogen peroxide as an oxidizing agent to detoxify hydrogen sulfide in environmental and industrial pollution control applications. Again using sulfur K-edge XANES spectroscopy as an analytical technique, the researchers found that with an excess of H_2O_2 , the products observed were elemental sulfur, polysulfides, thiosulfate and sulfate (Figure 4). However, when only a minimum of hydrogen peroxide was added, sulfoxylate ions were detected, suggesting that the oxidation process proceeds through this intermediate.

SOLID STATE PHYSICS AND MATERIALS SCIENCE

EXAFS techniques are heavily applied tools for the solid state physics and materials science fields. The standard techniques are now being complemented with experiments which make use of the polarization characteristics of synchrotron radiation: the linear polarization on-axis is exploited for directional sensitivity with single crystal and surface samples; the elliptical polarization off-axis is utilized in x-ray magnetic circular dichroism (MCD)

spectroscopy to provide information about magnetic structure. Again, there were a large number of important experiments, of which only a few can be highlighted here:

V. Harris, B. Das, N. Koon and W. Elam (NRL) studied the properties of "mixtures" of immiscible elements subjected to mechanical deformation on beamline X23A2. In an effort to unravel the structural effects occurring when elements which do not mix under equilibrium conditions are subjected to mechanical mixing, the researchers measured the EXAFS of $\text{Cu}_{70}\text{Fe}_{30}$ and $\text{Ag}_{70}\text{Fe}_{30}$ powders ball-milled under inert gas for varying times. The Fourier transforms of the Cu-Fe mix clearly demonstrate that after 20 hours of ball-milling, both Cu and Fe are in fcc sites (the iron starts as bcc) and are alloyed at the atomic level. In contrast, even after 200 hours of ball-milling the Fe in the Ag-Fe mix remains in a bcc phase, whereas the Ag is fcc (Figure 5). Little or no mixing has occurred.

A Sahiner, W. McCarroll, M. Greenblatt and M. Croft (Rutgers U.) have been correlating threshold features in the L-edge spectra of 4d metals with molecular orbital (band structure) symmetries and occupancies. They found, in measurements on beamline X19A, that the $L_{2,3}$ edges of molybdenum oxide complexes have two

"white line" features (dipole allowed $2p\text{-}3d$ absorption maxima at the edge) whose position and intensity track the energies and relative degeneracies of the t_{2g} and e_g levels as the valence state and symmetry of Mo is systematically altered. The features thus provide an extremely useful tool for monitoring the state of Mo in, for example, catalysts. The success of these studies motivated A. Sahiner, R. Herber, M. Croft and Y. Jeon (Jeonju U.) to pursue similar investigations into systematic variations in the K-edges of S and Cl ($1s\text{-}2p$), and L_1 -edge of I ($2s\text{-}5p$) complexes. It is found in these cases, however, that the areas of the "white lines" are a function not only of the number of available p-holes, but also reflect variations in the transition matrix elements. The energies of the principal absorption maxima also vary significantly with valence. Rutgers experimenters A. Sahiner, M. Cieplak, S. Guha, P. Lindenfeld, B. Bilash, and M. Croft also performed polarized XAS measurements on laser deposited high T_c films. The group studied the polarization dependence of the x-ray absorption spectrum at the Cu K edge of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films grown on a SrTiO_3 substrate. By orienting the sample such that the x-ray polarization vector was parallel or normal to the CuO_2 planes, the in- and out-of plane electronic states and coordination environments could be sampled separately. The sharpness of the polarized near-edge spectra are indicative of the high quality of the films produced via laser deposition techniques.

Y. Dao, A. Edwards, R. Nemanich, and D. Sayers (North Carolina State U.) performed experiments on titanium disilicide, a material suitable for contacts in VLSI circuits because of its low resistivity and thermal stability. Films of TiSi_2 can be grown by deposition of Ti on clean silicon, followed by an annealing process to yield a desirable C49 phase. If the anneal temperature is raised above 700°C , a phase transition occurs, however, yielding an undesirable C54 phase which is prone to islanding. In EXAFS measurements carried out at beamline X11A, the experimenters were able to confirm that the C49 phase could be thermally stabilized via the codeposition of Zr ($\text{Ti}_{1-x}\text{Zr}_x$), which only forms the C49 phase. Using the Fourier transforms as fingerprints, it was found that the C49-C54 transition temperature was raised about 200°C . Z. Wang, R. Nemanich and D. Sayers performed similar studies of reactions of Co deposited on Ge(100) and Si(100), finding evidence for a progression of phases as the annealing temperature is raised from 275°C to 775°C .

X. Yang, H. Lee and J. McBreen (BNL) and F. Lu (U. of Kentucky) studied a new class of electrolytes made up of potassium salts dissolved in poly(ethylene oxide) polymer. Though the polymer is immobile, from a macroscopic point of view, its interactions with the

potassium ions play a key role in the conduction process. Near-edge XAS studies carried out on beamline X19A revealed a number of interesting trends for salt/polymer systems with added plasticizers. J. McBreen also studied the underpotential deposited (UPD) monolayers of copper on carbon supported platinum in an acidic solution. The EXAFS experiments, carried out at beamline X11A, investigated the structure of the electrode/electrolyte interface to determine the mechanism allowing Cu to adsorb at potentials positive to the electrochemically reversible deposition potential. Analysis of the Cu first shell revealed the presence of three first shell oxygen atoms at 2.06 Å, a sulfur at 2.37 Å, and a Pt at 2.67 Å. This is interpreted to suggest that a bisulfate ion (HSO_4^-) binds atop the copper, which in turn binds atop a Pt atom on the electrode surface. The bisulfate ion probably facilitates the transfer of charge from the copper to the platinum, thereby giving the adsorbed UPD Cu^+ species observed with XANES spectra. J. McBreen, with D. Qu and B. Conway (U. of Ottawa) investigated MnO_2 , the active material in commercial alkaline batteries, to understand why addition of a small amount of Bi renders it rechargeable. From in-situ experiments performed on beamline X23A2, spectra of the Bi $L_{2,3}$ -edge and Mn K-edge clearly reveal that the Bi is reduced to Bi metal on deep discharge. In the charge cycle, the Bi is oxidized to Bi(III) prior to the onset of oxidation of the MnO_2 material. The results elegantly demonstrated the reversibility of the system throughout the charge/discharge cycle.

Q. Lu, B. Bunker, A. Kropf, K. Kemner (U. Notre Dame), R. Mayonovic (Southwest Missouri State U.), M. Gehrke (Lawrence U.), J. Buschert (Goshen College), and K. Zhang (U. Chicago) studied premelting near internal interfaces on beamline X11A using the variable penetration by x-rays at glancing angles to control the depth of probing. The group measured the XAFS of Cu at a buried $\text{Cu}/\text{Al}_2\text{O}_3$ interface produced by capping a thin Cu film on quartz with 700 Å of Al_2O_3 . By varying the angle, it was possible to sample depths from 10 to 50 Å. Early results showed the onset of large in-plane anharmonic motions in the top few layers at temperatures below the melting point, a hypothesis being tested further with concurrent XAFS and reflectivity measurements.

CATALYSIS AND CHEMISTRY

X-ray absorption techniques are also highly useful for characterizing catalysts and chemical reagents, and a number of research groups representing industry, universities, and government laboratories performed important experiments in the past year. Some selected highlights:

T. Stemmler and J. Penner-Hahn (U. Michigan), and P. Knochel (Philipps-Universität) have been studying

organo-cuprate complexes, among the most versatile of reagents for forming new carbon-carbon bonds, on beamlines X9B and X19A [see J. Am. Chem. Soc. **115**, 348 (1993)]. As with many reagents and catalysts, though their utility is well known, very little is known about their structures and reaction mechanisms. Recent crystal structures have revealed that both lower order (2-coordinate) and higher order (3-coordinate and higher) organocuprate anions can exist in the solid state. Studies of solution complexes made from the reactions of copper cyanide (CuCN) with both butyl lithium (BuLi) and Grignard reagents (BuMgBr) give identical results: only two-coordinate species of $\text{Cu}(\text{CN})\text{Bu}^-$ or CuBu_2^- exist, depending on stoichiometries. Thus, there is no evidence for higher order cuprates, suggesting that prevailing ideas of reaction mechanisms need re-evaluation.

S. Bare, G. Mitchell, and R. Moore (Dow Chemical) investigated the oxidation states of antimony in mixed antimony and tin oxides used as catalysts for the selective oxidation of olefins. A key step in the development of the catalyst is the enrichment of the catalyst surface with multivalent antimony cations. By studying the Sb L absorption edges of the catalyst along with a systematic series of model complexes on beamline X19A, the researchers were able to determine the relative amounts of Sb^{3+} and Sb^{5+} as a function of antimony loading (Figure 6). In near-edge studies on bimetallic Cu/Pt supported on activated carbon, S. Bare, L. Ito, and J. Maj worked to fully understand the chemistry involved in the pretreatment of this catalyst and in its activity in degrading chlorofluorocarbons. The Cu K-edge and Pt $L_{2,3}$ -edge XANES measurements demonstrate that hydrogen pretreatment of a catalyst precursor prepared from chloride salts on carbon reduces all Pt and Cu to the metallic state. Preliminary EXAFS results suggest that true bimetallic Cu-Pt particles are formed.

D. Liu and H. Robota (Allied Signal) studied the copper/ZSM-5 zeolite catalyst system on beamline X18B, its activity towards carbon monoxide (CO) and nitric oxide (NO), and the reduction of nitrogen oxides (NO_x) by hydrocarbons. In Cu K-edge measurements, CO, a major pollutant in the exhaust gas of lean-burn automobile engines, was found to react instantly with Cu(I) in prepared Cu/ZSM-5 catalysts at temperatures below 673 K. The shift in edge position suggests CO-to-Cu(I) charge transfer, an idea supported by observed changes in the CO infrared stretching frequency. Above 673 K, the CO appears desorbed. The Cu(II) form of the catalyst was found to not react with CO, except at elevated temperatures where it can reduce Cu(II) to Cu(I) or Cu(0). NO, another major constituent of the pollutants generated by combustion engines, is thermodynamically unstable com-

pared to oxygen and nitrogen gas, permitting the direct decomposition ($2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$). Until recently no suitable catalyst system has been known; however, the Cu/ZSM-5 system has been reported to show activity. After reductive preparation of the catalyst in an in-situ reactor, Cu(I) was observed. Variations in decomposition efficiency with temperature were found to correlate with the amount of Cu(I) present, supporting reaction models invoking Cu(I) as the active species. Addition of oxygen in the reactant stream suppressed both Cu(I) levels and NO decomposition. A further study revealed that the presence of hydrocarbon in even an oxidizing reaction

stream was enough to produce a measurable quantity of Cu(I) and result in NO conversion.

G. Lei, H. Trevino, and W. Sachtler (Northwestern U.) compared the local structure of Rh in zeolite Y as a function of the presence or absence of Mn ion and pH during catalyst preparation in experiments on beamline X18B. Manganese-promoted Rh/zeolite Y catalyzes the conversion of $\text{CO} + \text{H}_2$ to oxygen-containing compounds. The Rh K-edge EXAFS (Figure 7) reveals significant outer shell backscattering from the zeolite framework for samples prepared in the absence of Mn, whereas this is attenuated when Mn ion is added at low pH (6.5). This is interpreted to reflect Mn^{2+} competing for hexagonal prism sites, leaving more Rh in sodalite or supercage sites where backscattering from the framework is expected to be weaker. After reduction of the metal/zeolite system at 200°C , rhodium clusters are formed. By estimating the size of the clusters from the magnitude of the Rh-Rh coordination shell, the researchers conclude that Rh^{3+} in prism sites is hardly reduced, whereas Rh in supercages is easily reduced to Rh^0 and can form clusters.

W. Kawi, J. Chang, and B. Gates (U. Delaware) studied the structure and stability of a supported metal cluster as it catalyzed the hydrogenolysis of propane ($\text{C}_3\text{H}_8 + 2\text{H}_2 \rightarrow 3\text{CH}_4$) at 200°C on beamline X11A. Ir_4 clusters were prepared on MgO powder via the decarbonylation of a metal-carbonyl cluster precursor. Freshly prepared and "used for one day" catalysts were both characterized by Ir-Ir coordination numbers of ~ 3 , as revealed by EXAFS measurements, supporting the model of stable, tetrahedral Ir_4 clusters. The researchers suggest this to be the first report of the catalytic activity of a well-defined, supported metal cluster.

J.J. Rehr, S. I. Zabinsky, and A. Ankudinov (U. Washington) and R.C. Albers (Los Alamos) released FEFF6.0x, the polarized, multiple scattering version of the XAFS simulation program, in 1993. The FEFF programs have become an integral part of the data analysis process for many researchers, and the addition of accurate simulations of polarization dependent EXAFS for atoms in and beyond the first shell is a welcome advance. The EXAFS analysis package for the Macintosh developed by L. Furenlid (NSLS), C. Bouldin (NIST) and T. Elam (NRL) was upgraded to version 3.2. Current versions are freely available via anonymous ftp from the EXAFS database at IIT (ftp to xafsd.b.iit.edu, login as "ftp", any password OK).

X-ray absorption spectroscopy continues to be a strong synchrotron science at the NSLS, with a steady progression of incremental and innovative developments in beamlines, techniques, and theory.

X-RAY EMISSION SPECTROSCOPY

Y. Ma

Pacific Northwest Laboratory and U. of Washington

X-ray emission experiments using monochromatic photon excitation continue to be performed at the NSLS with some very interesting results. In last year's NSLS Annual Report (1992), I discussed evidence which suggests that the excitation-emission process should be treated as an inelastic scattering event. There are two significant consequences to this scattering picture. The first one says that the emission spectral lineshape should show strong excitation energy dependence. This was first observed at the Si L-edge in crystalline Si and at the C K-edge of diamond, as reported in last year's NSLS Annual Report (1992). Peter Johnson (BNL Physics) and Yanjun Ma (U. of Washington) have performed a band structure calculation based on the inelastic scattering approach which shows results which are in good agreement with the experimental observations. An excitation energy dependence is observed also at the C K-edge of graphite, as shown in Figure 1. These emission spectra were taken using the intense X1B soft x-ray undulator beamline and the Uppsala soft x-ray spectrometer. Using polarization dependence, the emission spectra can be separated into their σ and π components, each of which shows an excitation energy dependence in the spectral lineshape.

Excitation energy dependence of the emission process was also used by J.-E. Rubensson, S. Eisebitt, M. Nicodemus, T. Böske, and W. Eberhardt (Forschungszentrum Jülich, Germany) to study the $\text{Ca } 3s^{-1}3d$ states in CaF_2 . The $3s^{-1}3d$ state is created by a two-step process: a Ca 2p electron is promoted to a 3d level by a soft x-ray photon and the 2p hole is filled by fluorescent decay of a 3s electron. The final $\text{Ca } 3s^{-1}3d$ configuration gives rise to four states, split by the 3s3d exchange interaction and the crystal field. The emission spectra (Figure 2) were taken at beamline X1B with the new Jülich Rowland circle soft x-ray spectrometer. Using the depen-

Figure 1 X1B: (top) C K-edge absorption spectrum of highly oriented paralytic graphite (HOPG). The peak at 286 eV (292 eV) corresponds to final states of $\sigma(\pi)$ symmetry. (bottom) CK-emission spectra of HOPG excited with monochromatic soft x-rays at different energies. From the polarization dependence, the σ (left) and π (right) symmetry states can be separated. P. Skytt, N. Wassdahl, P. Glans, J. Guo, D.C. Mancini, J. Nordgren (Uppsala U.) and Y. Ma (U. of Washington).

Figure 2 X1B: Ca core-to-core fluorescence spectra from CaF_2 excited at the photon energies indicated (in eV) on the right hand side of each spectrum. The x-axis scale is a "binding energy" determined by subtracting the excitation energy from the emission energy. Four solid vertical lines mark the $3s-3d$ final states. At 349.0 eV and 352.3 eV excitation energy, the states of t_{2g} symmetry are emphasized, whereas the other excitation energies emphasize e_g symmetry. The states are, in order of increasing binding energy, 3E_g , 1E_g , $^3T_{2g}$, and $^1T_{2g}$. See J.-E. Rubensson, S. Elsebitt, M. Nicodemus, T. Böske, and W. Eberhardt, *Phys. Rev. B* **49**, 1507 (1994).

Figure 3 X24A: Si K-emission spectra of silicon taken at several incident photon energies near the Si K-absorption edge. The spectra were obtained from Si samples of (111), (110), and (100) orientation under identical experimental conditions, i.e. excitation energy, take-off angle, and spectrometer settings. The dependence on sample orientation demonstrates the anisotropy predicted by inelastic scattering theory. Y. Ma (U. of Washington), K.E. Miyano (Brooklyn College), P.L. Cowan (NAL), and Y. Aglitzky and B.A. Karlin (NIST).

dence of the emission spectra on excitation energy, the final states could be fully assigned and thus the magnitude of the $3s3d$ exchange interaction and the crystal field splitting could be determined. The major conclusion from this work is that those Ca d-orbitals in CaF_2 which are directed towards the F atoms (orbitals of t_{2g} symmetry) have a larger exchange interaction with the Ca $3s$ electron than those directed in the space between F atoms (orbitals of e_g symmetry).

The second prediction of the inelastic scattering approach is the angular dependence of emission spectra obtained with monochromatic photon excitation. This anisotropy exists even for cubic materials, and therefore has a different physical origin from the polarization dependence of anisotropic materials. Yanjun Ma (U. of Washington), Ken Miyano (Brooklyn College), Paul Cowan (ANL), Y. Aglitzky and B.A. Karlin (NIST) have observed this anisotropy at the Si K-edge on X24A (Figure 3) using a bent crystal spectrometer built by R.D. Deslattes

et al. (NIST). This observation of anisotropy provides the strongest proof to date for the resonant inelastic scattering interpretation of the excitation-emission process.

The C $1s$ core exciton of diamond has been a subject of recent debate. The core exciton problem is related, via the equivalent core approximation, to the important problem of nitrogen doping impurities in diamond. Y. Ma (U. of Washington) and P. Skytt, N. Wassdahl, P. Glans, D.C. Mancini, J. Guo, and J. Nordgren (Uppsala U.), have investigated the C K-edge core excitons in diamond (Figure 4) and graphite. Using intense monochromatic soft x-ray photon excitation provided by the X1B beamline, they were able to observe the core exciton in the emission spectra, which has not been possible previously using electron excitation. This method of studying the core exciton decay process offers new insight into the core exciton problem. They found strong vibronic coupling effects in the core exciton emission spectrum. Simple Franck-Condon analysis has produced

Figure 4 X1B: (a) C K-edge absorption (dashed) and emission (solid curves) spectra of diamond. The emission spectra are measured with excitation energy of 289.6 (curve 1) and 294.5 eV (curve 2), respectively. (b) The absorption and emission spectra in the band-gap region: Experimental emission (filled diamonds) and absorption (open diamonds) spectra. The solid line represents the Franck-Condon phonon spectrum calculated with $Q_0=0.2\text{\AA}$ and $n=8$, and broadened by a Gaussian of $\text{FWHM}=0.9\text{ eV}$. The dashed curve represents the phonon broadened excitation peak with $Q_0=0.2\text{\AA}$. Y. Ma (U. of Washington) and P. Skytt, N. Wassdahl, P. Glans, D.C. Mancini, J. Guo, and J. Nordgren (Uppsala U.). See Phys. Rev. Letters 71, 3725 (1993).

Figure 5 X25: (a) Mn K β emission spectra from compounds of Mn(II) and Mn(IV), and a physical mix of the two. (b) X-ray absorption near edge spectra of the above samples taken with the high resolution fluorescence yield method, where only fluorescence intensity from appropriate emission energies is monitored. X. Wang, M.M. Grush, G. Peng, S.P. Cramer (U. California Davis), J. Moore (LBL), and K. Hämäläinen (NSLS, U. Helsinki).

new estimates for the core exciton binding energy and the magnitude of the Jahn-Teller distortion of the core exciton state.

It is well known that the core level binding energies of atoms are sensitive to their chemical environments. This is the basis for the Electron Spectroscopy for Chemical Analysis (ESCA) technique. It is not well known, however, that the x-ray emission lines are also sensitive to the chemical environment, such as the oxidation state of an atom in a solid. Using the focused wiggler beamline X25, X. Wang, M.M. Grush, G. Peng, S.P. Cramer (U. California Davis), J. Moore (LBL), and K. Hämäläinen (NSLS, U. Helsinki) demonstrated that the Mn K β emission line positions and intensities are dependent on the oxidation states of the Mn atoms (Figure 5a). Furthermore, by monitoring the fluorescence yield at specific

fluorescence energies, they demonstrated that it is possible to perform oxidation state specific absorption experiments (Figure 5b).

X-ray resonant Raman scattering fine structure was observed near the Ni K edge of NiO by C.-C. Kao, K. Hämäläinen, M. Krisch, D.P. Siddons, and J.B. Hastings (NSLS). The experiment was performed at the X21 hybrid wiggler beamline with total energy resolution about 1 eV. Figure 6 shows a series of resonant Raman spectra taken at incident photon energies near the Ni K absorption edge (around 8340 eV). The energy range of the spectra was chosen to be close to the Ni K β fluorescence line. At an incident energy of 8400 eV, roughly 60 eV above the absorption edge, the spectrum is essentially the Ni K β fluorescence spectrum of NiO. However, as the incident photon energy is lowered towards the Ni K

Figure 6 X21: Series of x-ray resonant Raman spectra of NiO taken at incident photon energies near the Ni K absorption edge, revealing previously unobserved fine structure. The total energy resolution was approximately 1 eV. C.-C. Kao, K. Hämäläinen, M. Krisch, D.P. Siddons, and J. B. Hastings (NSLS).

Figure 7 X21: Dispersion of the resonant x-ray Raman scattering features labeled A to E in Figure 6 with incident photon energy, showing the expected linear dependence.

absorption edge and below, a new set of spectral features emerges. Five distinct features can be identified in the spectra, and are labeled from A to E in Figure 6. These features can be shown to correspond to features in the absorption fine structure of NiO near the Ni K edge. They also clearly show linear dispersion with the incident photon energy as expected from the resonant Raman process. Figure 7 shows the dispersion of A to E with the incident photon energy.

There are several advantages of measuring the near edge absorption fine structure using resonant Raman scattering: the lifetime width of the core hole is eliminated from the spectra; the signal-to-background ratio is better; there is no need to scan the incident beam energy in the measurement; and there is no need to correct for saturation effects or self-absorption effects. Furthermore, with the improved energy resolution demonstrated here, many-electron effects in the resonant Raman process may be observed.

X-RAY SCATTERING AND CRYSTALLOGRAPHY

Lonny Berman
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NSLS

SURFACE STUDIES

Highlighting surface x-ray diffraction were two temperature-dependent studies of phase transformations of clean surfaces in ultrahigh vacuum (UHV). The critical behavior of the (3×1) reconstruction of the Si(113) surface, as it disorders above the 959K transition temperature, was studied by D.L. Abernathy, R.J. Birgeneau, K.I. Blum, and S.G.J. Mochrie in a custom chamber at X25 [work published in Phys. Rev. Lett. **71**, 750 (1993)]. They measured the temperature dependences of (3×1) superlattice peak widths, positions, and intensities above the critical point to determine critical exponents for the inverse correlation lengths, incommensurability, and susceptibility, respectively, of the reconstructed surface layer (Figure 1). The results suggest that this continuous commensurate-to-incommensurate transformation falls within a new chiral melting universality class, with an unusual anisotropic scaling of the correlation lengths above the critical point. The exponents do not agree with those suggested by conventional theories (dashed lines in Figure 1). This experiment demonstrates that high-resolution critical x-ray scattering studies can yield new insight into the nature of continuous phase transitions in two dimensions.

A temperature-dependent study of faceting transformations of a stepped Pt(001) surface in UHV, by G.M. Watson, D. Gibbs, D.M. Zehner, M. Yoon, and S.G.J. Mochrie at X20A and X22C [work published in Phys. Rev. Lett. **71**, 3166 (1993)], revealed a rich temperature-orientation phase diagram. High-resolution x-ray diffraction scans showed that above 1820K, a single rough phase with an average surface oriented along the macroscopic miscut direction (1.4° away from the (001) direction) exists. Between 1820K and 1620K, unstepped, hexagonally reconstructed (001) facets coexist with stepped, unreconstructed regions; the tilt angle of the stepped domains has a one-half power-law dependence on reduced temperature (Figure 2), which further supports the identification of the high-temperature vicinal surface as rough. Finally, below 1620K, the rough stepped domains transform to stepped domains in which the terraces

Figure 1 X25: (a) Incommensurability (ϵ), inverse correlation lengths κ_x, κ_y , (b) susceptibility (χ), square of the order parameter (I_0), (c) $R_s = \chi \kappa_x \kappa_y / I_0 V_r$, where V_r is the two-dimensional resolution volume, and (d) $\omega_0 = \epsilon / \kappa_x$ versus reduced temperature $\tau = (T - T_c) / T_c$. Circles correspond to the high-resolution and squares to the low-resolution configuration. Triangles are a combination of low- and high-resolution data from above and below T_c . The fact that the R_s ratio is constant shows that the exponents obey a hyperscaling relation predicted by theory. See D.L. Abernathy, R.J. Birgeneau, K.I. Blum, and S.G.J. Mochrie (MIT), Phys. Rev. Lett. **71**, 750 (1993).

reconstruct to form a buckled, rotated hexagonal structure, with the buckling crests and troughs running parallel to the step edges. Below 1500K, the terrace width locks in to four times the buckling period. This represents the first observation of a magic vicinal, for which the step period is commensurate with the reconstruction period. This experiment highlights the use of x-ray scattering to elucidate the thermodynamics of surface morphology.

X-ray standing wave studies of surfaces continue to be useful in determining locations of adsorbed atoms. Recent experiments by G.E. Franklin, Y. Qian, M.J. Bedzyk, J.A. Golovchenko, J.C. Woicik, E. Fontes, and J.R. Patel at X15A have focussed on submonolayers of As, Bi, and Ga adsorbed on the Si(100) surface in UHV. These adsorbates all form dimers when deposited on this surface, similar to the first-layer dimers of the clean surface itself. Standing wave measurements as functions of coverage and temperature using different sets of Bragg planes were used to determine the height, buckling, bond length, vibration amplitude, and degree of order of the dimers. All of the dimer species were determined to be symmetric, with the As and Bi dimers being more ordered and stable than Ga dimers. The dimer bond lengths and heights were determined with extremely high precision, as small as $\pm 0.01\text{\AA}$. Typical results, for Ga on Si(100), are shown in Figure 3. A temperature-dependent standing wave study of the As vibrational amplitude on the Si(100) surface showed the mean-squared amplitude to be consistent with the harmonic approximation of the Debye model up to 650K, but rapidly increasing at higher

temperatures; this behavior has not been predicted theoretically. These experiments highlight the applicability of x-ray standing wave studies to quantify adsorbate site locations, symmetries, and lattice dynamics.

X-ray scattering studies of two-dimensional structures have not been confined to surfaces in UHV. X-ray reflectivity and diffraction were used by X.Z. Wu, E.B. Sirota, S.K. Sinha, B.M. Ocko, and M. Deutsch at X22B to determine the surface structure of organic liquids, specifically n-alkanes (waxes), which form the major constituents of oils, fuels, polymers, and lubricants [first results published in *Phys. Rev. Lett.* **70**, 958 (1993)]. They found that the top layer of the liquid crystallized at temperatures as high as 3K above the bulk solidification temperature, for hydrocarbon chain lengths n between 16 and 50. The chains in this "solid" surface layer were determined to be hexagonally packed and pointing perpendicular to the surface, with a density higher than that

Figure 2 X20A, X22C: Temperature dependence of the domain tilt angles on the stepped Pt(001) surface, measured using high resolution x-ray diffraction. See G.M. Watson, D. Gibbs (BNL Physics), D.M. Zehner (ORNL), M. Yoon, and S.G.J. Mochrie (MIT), *Phys. Rev. Lett.* **71**, 3166 (1993).

Figure 3 X15A: Measured position coordinates for the parallel ad-dimer model of the Si(100)2x2:Ga surface, from an x-ray standing wave study by Y. Qian, M. J. Bedzyk (ANL and Northwestern) and G. E. Franklin (Harvard). The dashed lines are the Si(400) bulk-extrapolated lattice planes. L represents the Ga ad-dimer bond length and h' is the height of the Ga dimer above the bulk-extrapolated lattice plane. The table lists L , h' , and C (the Ga ordered fraction) for five Ga coverages Θ , in monolayers.

Figure 4 X22B: (a) X-ray reflectivity from three liquid n-alkanes ($n=18, 20$, and 24), shifted by two decades each for better visibility. Open circles: liquid surface phase, open squares: surface monolayer phase. Inset: surface electron density profiles for one-slab (thick line) and two-slab (thin line) models. The depletion layer is clearly seen.

(b) In-plane diffraction scans of the $n=20$ alkane liquid. At high temperature, only the liquid bulk peak (open circles) is observed. The formation of the surface crystalline monolayer is manifested by a drop in intensity of the liquid peak and the appearance of a resolution-limited Bragg peak (solid circles). See X.Z. Wu, E.B. Sirota, S.K. Sinha, B.M. Ocko, and M. Deutsch, *Phys. Rev. Lett.* **70**, 958 (1993).

of the bulk liquid (Figure 4). The formation of the ordered surface layer was found to be abrupt at the transition temperature, showing the transition to be first-order. These results were correlated with surface tension measurements. This layering transition did not occur for chain lengths shorter than 14, indicating perhaps a change in the surface behavior from one of surface freezing upon cooling (for the longer lengths) to surface melting upon warming (for the shorter lengths). This work represents the first observation of surface-induced ordering in simple molecular liquids.

DIFFUSE SCATTERING

X-ray diffuse scattering from a single crystal of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ was studied in the vicinity of several Bragg peaks at X25 by W. Dmowski, R. McQueeney, T. Egami (U. of Pennsylvania), Y. P. Feng, S. K. Sinha (Exxon), D. E. Moncton (APS, ANL), T. Hinatsu, and S. Uchida (U. Tokyo). In addition to thermal diffuse scattering (TDS), anisotropic, temperature dependent diffuse scattering was observed (Figure 5). The measurements were performed as a function of temperature from 10K up to 300K. The diffuse scattering at 300K (Figure 5a) is found to be explained well by TDS due to phonons calculated with the shell model fitted to the dispersion curves determined by inelastic neutron scattering. However, below 200K extra diffuse scattering (EXDS) develops (Figure 5b), and its intensity gradually increases with decreasing temperature and saturates below 100K. The orientational analysis of EXDS shows that it is mostly due to localized transverse displacement fields. The EXDS intensity strongly depends on the reduced wavevector q , with the power law close to -4 , and is anisotropic within the x - y plane, containing a strong component with $(d_{xy})^2$ symmetry. Its intensity and temperature dependence suggests that the EXDS is not related to the tetragonal/orthorhombic phase transition, nor due to lattice defects including surfaces.

CHARGE FLUCTUATION SCATTERING

Two experiments measured the responses of charge density wave (CDW) superlattice Bragg reflections to applied electric fields. Measurements of CDW peak intensities and electric currents at different temperatures, in response to an applied electric field, in the one-dimensional conductor $\text{K}_{0.3}\text{MoO}_3$ (blue bronze) by J. Zhang, J.F. Ma, S.E. Nagler, A. Garrett, and S.E. Brown at X16B and X20C [first results published in *Phys. Rev. Lett.* **70**, 3095 (1993)] showed a one-to-one correlation between the time dependence of the peak intensity and the transient of the electric transport (Figure 6) at late times. A percolation response model based on distinct relaxation

rates for individual domains fits the transient response slightly better than a stretched exponential function.

At X25, the kinetics of sliding charge density waves in NbSe_3 were measured by E. Sweetland, A.C. Finnefrock, K.L. Ringland, and J.D. Brock. The CDW superlattice peak intensity, position, and lineshape were measured in

response to alternating driving electric fields for samples with varying Ta impurities. The observed time scales of the CDW strain field response were found to depend strongly on the impurity concentration, and ranged from less than 1msec for very pure crystals (Figure 7) to a few seconds for heavily-doped samples.

Figure 7 X25: (left) Experimental arrangement, showing electrical connections and x-ray scattering geometry. E. Sweetland, A.C. Finnefrock, K.L. Ringland, and J.D. Brock (Cornell).

(right) Measured charge density wave (CDW) peak intensity vs. time from a very pure crystal of NbSe₃, in response to the driving field shown in the inset.

MAGNETIC SCATTERING

Experiments at X14A by E.D. Isaacs, P. Zschack, B.D. Gaulin, J.G. Lussier, A. Schröder, L. Taillefer, H. Williams, C. Oglesby, and E. Bucher took advantage of resonant enhancement of the magnetic scattering cross section at U M-edges to learn about the magnetism in heavy fermion uranium-based superconductors. One study revealed the orientation of the magnetic moment in UPd₂Al₃ by observing the intensity modulation of a magnetic Bragg peak while the sample was rotated azimuthally about the scattering wave vector. A second study correlated the antiferromagnetic order with the onset of superconductivity in UPt₃, by measuring the temperature dependences of a magnetic Bragg peak intensity and width in the vicinity of the superconducting transition temperature. The magnetic Bragg intensity was observed to grow from zero at 5K to a maximum at the 0.6K transition temperature, then drop as the temperature was lowered further (Figure 8). This change

Figure 8 X14A: Temperature dependence of the integrated intensity of the (1/2, 0, 2) magnetic Bragg peak in UPt₃, where T=0.6K was the measured superconducting transition temperature. Solid line: line fits to the data above and below T=0.6K. Inset: $\theta/2\theta$ scan through the (1/2,0,2) magnetic Bragg peak (filled circles), giving an inverse correlation length of 0.013 Å⁻¹. Open circles: the higher-order ($\lambda/4$) component for the same scan. E.D Isaacs (AT&T), P. Zschack (ORISE), C. Oglesby (AT&T) and E. Bucher (AT&T and U. Konstanz).

of behavior could arise from a rotation of the ordered magnetic moment as the temperature was reduced below T_c , or from a suppression of the size of the moment. These measurements may shed light on the interplay between superconductivity and antiferromagnetism in heavy fermion superconductors. These studies also posed a serious experimental challenge, since the absolute temperature was required to be scanned below 1 K while the sample was rotated on the diffractometer. A custom helium dilution cryostat compatible with a Huber diffractometer was constructed for this purpose.

COHERENT BEAM DIFFRACTION

X-ray speckle was observed in the specular reflection of coherent x-rays from islands of gold-coated films of symmetric diblock copolymers of polystyrene and polymethylmethacrylate (PMMA), by Z. Cai, B. Lai, W. Yun, I. McNulty, K. Huang, and T.P. Russell at X6B. A small pinhole was used to select a spatially coherent beam at 6 keV. The speckle patterns were recorded by a charge-

coupled device (CCD) detector. Figure 9 shows line profiles of the CCD intensity along the takeoff angle direction, using pinholes of diameter 5, 12, and 60 μm respectively; the intensity at the specular position was occluded to prevent saturation of the detector. The speckle is represented by the fluctuations in the beam intensity, and becomes more visible as the pinhole diameter is decreased (i.e., as the beam becomes more coherent). The speckled reflected intensity arises from interference of the beam components scattered by different islands; island length scales of up to 150 μm were identified. Speckle was not observed from an annealed film of gold on polystyrene and PMMA which was devoid of islands. This experiment highlights the use of coherent beam reflectivity to study inhomogeneities of surfaces and interfaces of non-crystalline materials.

PROTEIN CRYSTALLOGRAPHY

Multiple-wavelength anomalous dispersion (MAD) was used at X12C by V. Ramakrishnan, J.T. Finch, V.

Graziano, P.L. Lee and R.M. Sweet to solve the structure of a protein involved in DNA binding [work published in *Nature* **362**, 219 (1993)]. The genome of higher organisms is organized as chromatin, a complex of DNA with proteins called histones. The basic subunit of chromatin is the nucleosome, a complex of eight core histones around which are wrapped about two turns of DNA. The linker histone H5 binds to the nucleosome and helps to organize the nucleosomes into a larger, 30nm thick filament. The interaction between the linker histone and chromatin is interesting for both structural reasons and because it may help control the transcription of genes.

MAD measurements around the selenium K-edge on a crystallized protein consisting of a cloned gene for the central globular domain (GH5) of H5, in which selenium was substituted for sulfur, were used to determine the structure shown in Figure 10. Despite very little similarity in amino-acid sequences, the structure shows a striking similarity to those of other proteins that belong to the helix-turn-helix class of DNA binding proteins. This immediately suggests a mode of DNA binding for GH5. A second DNA binding site has also been tentatively identified.

CRYSTALLOGRAPHY (OTHER THAN PROTEINS)

Anomalous scattering continues to be used to solve intractable problems in crystallography. An example of this was an experiment performed by Coppens and co-workers on beamline X3. They studied a single-crystal sample of a mixed valence compound μ -dioxo-(Mn(2,2'-bipyridyl)₂)(BF₄)₃·3H₂O. This is a model compound for the oxygen-evolving center in green plants (Photosystem II). This study was particularly noteworthy since it took advantage of two key features of synchrotron radiation, tunability (to distinguish between the different oxidation

states of the Mn sites by near-edge differences) and polarization (to determine the orientation of the transition moment integral vector).

Another experiment to make use of anomalous scattering was reported by H. Rhuizhong, T. Egami, A.-P. Tsai, A. Inoue, and T. Masumoto on beamline X7A. [see *Physical Review* **B46**, 6105 (1992)]. They studied samples of Al₆₅Ru₁₅Cu₂₀, a quasicrystal, using powder diffraction. By making measurements near the Ru and Cu edges they were able to make one of the first detailed structural determinations including chemical order in a quasicrystal. The same group also performed studies of local structure in the decagonal quasicrystal Al-Cu-Co. They were able to gain clarification of the nature of the structural defects in such materials by using a position sensitive detector (PSD) and analyzing the diffuse scattering in addition to the diffraction peaks.

A.P. Jephcoat, J.A. Hriljac and D.E. Cox studied the phase transitions occurring in C₆₀ at elevated pressures. They found that the results obtained were greatly dependent on the pressure-transmitting medium employed, a result which they attribute to the differing abilities of the various fluids to intercalate the C₆₀ structure.

An interesting application of powder diffraction which makes use of the high brightness of synchrotron radiation was a study of residual stress in a metal-ceramic joint by X.-L. Wang, T.R. Watkins, C.R. Hubbard, P. Zschack and M. Nelson on beamline X14. They were able to map the strains in different joint structures and compare them with finite-element model results.

P. Norby, A.N. Christensen and J.C. Hanson were able to follow the synthesis of an industrially important zeolite, Na-LTA, using the facilities at beamline X7B. They have a 120-degree PSD which allowed them to observe a large number of lines simultaneously with 1-

second time resolution. They were able to follow the reaction from an amorphous phase through the zeolite phase to the sodalite phase. Other studies involved the thermally induced transformations and dehydration reactions at temperatures up to 800°C (Figure 11).

It is in general noticeable that an increasing number of a wide variety of industrially important experiments are being performed at NSLS. These include many studies of the structure of various catalysis systems using the whole range of synchrotron radiation techniques, spectroscopic as well as crystallographic.

SMALL-ANGLE SCATTERING

Some interesting ideas on alternative instrumentation for small-angle scattering were examined by Knapp and his collaborators on beamline X6B. They used various combinations of curved crystals and 1-dimensional PSD's to achieve the good signal-to-noise ratio characteristic of crystal analyzer techniques while maintaining high throughput typical of imaging-type instrumentation (Figure 12). On beamline X12B, Capel has demonstrated successful operation of a millisecond time resolution stopped-flow solution scattering apparatus. This opens up the possibility of kinetic studies of macromolecular assembly and protein folding/unfolding.

OTHER

Bergmann and collaborators have demonstrated that high-precision measurements of the Lamb-Mössbauer factor can be made in a much more straightforward manner using synchrotron radiation than with a conventional radioactive source. Using beamline X25, they made measurements of the time-dependent forward scattering from an iron foil as a function of temperature. The improved precision comes from the fact that there is no need to measure absolute intensities and that the properties of the source are well-defined and simple (see discussion in the Time-Resolved Spectroscopy section).

K. Joensen, D. Graessle, K. Flanagan, A. Szentgyorgin, A. Kenter, P. Gorenstein, P. Hoghoj and P. Siddons studied the performance of some graded-spacing multilayers which are intended for use as supermirrors in x-ray telescopes. They were able to make reflectivity and diffuse scattering measurements at energies up to 35keV on beamline X27C, and demonstrated that good reflectivity over a large angular range was possible (Figure 13).

Also on beamline X27C, was an interesting study of x-ray propagation through an x-ray waveguide. The waveguide consisted of a thin polymer layer sandwiched between a silicon substrate and a silicon overlayer. Coupling into the waveguide was achieved through a stepped structure at the input end (Figure 14).

Figure 13 X27C: The reflectivity of a Ni/C variable d-spacing multilayer at 35keV incident photon energy. K. Joensen, D. Graessle, K. Flanagan, A. Szentgyorgin, A. Kenter, P. Gorenstein (Harvard Smithsonian Astrophysical Observatory), P. Hoghoj (ESRF) and P. Siddons (NSLS).

Figure 14 X27C: (left) The structure of the x-ray waveguide

(right) the mode structure measured in the far field excited in this structure. Interferences among all possible guided modes can be seen. Y. P. Feng (Exxon), D. P. Siddons (NSLS), S. K. Sinha (Exxon), H. W. Deckman (Exxon) and J. B. Hastings (NSLS).

X-RAY TOPOGRAPHY

Michael Dudley

SUNY at Stony Brook

Special Interest Group Representative

This report outlines significant scientific results obtained by the two beamlines mainly comprising the x-ray topography SPIG, i.e. X19C and X23A3, in that order.

A broad range of experiments has been carried out on X19C in the last year. In a collaborative program between Grumman Corporate Research Center (Grumman CRC) and M. Dudley's Group at SUNY Stony Brook, much progress has been made regarding the characterization of the MBE growth of CdTe buffer layers. M. Dudley and T. Fanning (SUNY-Stony Brook) and M. B. Lee and L. Casagrande (Grumman) correlated the detailed microstructures observed in the substrates with those observed in the epilayers. Detailed analysis was also performed of Te inclusions and dislocation cell structures in crystals that had been thinned down to

around $30\mu\text{m}$. An example is shown in Figure 1. This research demonstrates that topography is an ideal technique for screening CdTe substrates to optimize epilayer quality, and for characterizing the three dimensional distribution of defects in the epilayers.

D. Gillies, C.H. Su, A. Lehoczy, F. Szofran, and M.P. Volz of NASA Marshall Space Flight Center, in a collaborative program with M. Dudley, W. Zhou and G.-D. Yao of SUNY-Stony Brook have been using white beam topography at X19C to investigate defect structures in crystals used in electronic and photonic applications. Crystals investigated include ZnTe, CdTe and PbSe. As shown in Figure 2, twins, slip dislocations and growth dislocation networks have been observed. This work has shown that the detailed microstructural evolution of crystals can be determined from analysis of post-growth

Figure 1 X19C: White beam transmission topograph ($g=3\bar{1}1$, $\lambda=0.55\text{\AA}$) of a $30\mu\text{m}$ thick CdZnTe crystal showing individual dislocations comprising a cell structure and the significant lattice rotation associated with a Te precipitate. See T. Fanning, M.B. Lee, L.G. Casagrande, D. DiMarzio, and M. Dudley, *J. Electronic Materials* **22**, 943 (1993). Research funded by Grumman CRC.

Figure 2 X19C: White beam transmission topograph of a ZnTe crystal showing dislocation cell structures, slip bands, and twins. See W. Zhou, J. Wu, and M. Dudley, *Mat. Res. Soc. Symp. Proc.* **307**, 299 (1993). Research funded by NASA Marshall Space Flight Center contract NAG8-891.

topographs. In a similar program also funded by NASA, D. Larson of Grumman CRC and M. Dudley, G.-D. Yao and J. Wu of SUNY-Stony Brook have been comparing defect structures in CdZnTe crystals grown on earth to those grown in a microgravity environment on Shuttle mission STS-50. White beam topography has been used to examine as-grown boules and slices cut from the boules. An example of a topograph recorded from an as-grown boule is shown in Figure 3.

D. Larson, R. Silberstein and D. DiMarzio of Grumman CRC and M. Dudley and J. Wu of SUNY-Stony Brook, in a joint project funded by ARPA, have been using white beam topography at X19C to screen CdZnTe wafers to be used as substrates for I.R. focal plane arrays.

L.K. Cheng and J. Bierlein of DuPont, in a collaborative program with M. Dudley and S. Wang of SUNY Stony Brook, have been using white beam topography at X19C to investigate growth defect structures in KTA and KTP crystals, both of which have interesting optical properties. Dislocations, growth sector boundaries, inversion twin lamellae and ferroelectric domains have been observed and characterized. White beam section topography has been used to perform detailed analysis of lamellar ferroelectric domains (inversion twins). An example of a section topograph showing the classic "hourglass" contrast from such domains, along with the corresponding projection topograph, is shown in Figure 4. The influence of these defect structures on optical properties is being investigated.

Figure 3 X19C: Whole boule topograph, recorded in reflection geometry, from a CdZnTe boule grown by D. Larson of Grumman CRC on Shuttle Mission STS-50. Funded by NASA contract NAS8-38147.

Figure 4 X19C: (a) Synchrotron white beam section topograph (micro-slit width $15\mu\text{m}$, $g=101$, $\lambda=0.51\text{\AA}$) recorded in transmission geometry from a flux-grown KTP single crystal showing the classic "hour-glass" contrast from an inversion twin lamella, (b) the corresponding projection topograph recorded with the same reflection vector showing the expected fringe contrast. See S. Wang, M. Dudley, L.K. Cheng and J.D. Bierlein, Mat. Res. Soc. Symp. Proc. **307**, 243 (1993). Research funded by DuPont.

C. Fazi of Army Research Laboratory (Adelphi) and M. Dudley and S. Wang of SUNY- Stony Brook have continued to make excellent progress in their joint project at X19C investigating breakdown damage in semiconductor crystals. Details of the distribution of damage following reverse bias failure have been revealed. In a recent extension of this program, C. Carter and D. Asbury of Cree Research Inc. have joined us in an investigation of defect structures in very high quality SiC crystals grown at Cree. An example of a topograph recorded in the back reflection geometry showing a typical superscrew dislocation configuration in a SiC wafer is shown in Figure 5.

W.T. Pike of Jet Propulsion Labs, in a collaborative program with M. Dudley and J. Wu of SUNY-Stony Brook have been investigating relaxation processes in SiGe film growth using white beam topography at X19C.

I. Baker and F. Liu of Dartmouth College, jointly with M. Dudley at SUNY Stony Brook have been using white beam topography at X19C to investigate defect behavior in polycrystalline ice. Recently, the dynamics of faulted and unfaulted interstitial dislocation loops were investigated. An example of a topograph showing these loops is presented as Figure 6.

Figure 5 X19C: White beam topograph ($g=00036$, $\lambda=0.82\text{\AA}$) of a 6H-SiC crystal grown by Cree Research Inc., showing superscrew dislocations of varying Burgers vector magnitude and sign (the white circular features of different diameter), and faint images of basal plane dislocations. See S. Wang, M. Dudley, C. Carter Jr., D. Asbury, and C. Fazi, *Mat. Res. Soc. Symp. Proc.* **307**, 249 (1993). Research funded by Cree Research Inc.

Figure 6 X19C: White beam transmission topograph ($g=1\bar{1}01$, $\lambda=0.84\text{\AA}$) recorded from part of an ice bicrystal showing faulted and unfaulted interstitial dislocation loops generated by rapid cooling. Research funded by ARO grants DAAL03-92-G-0319 and DAAH04-93-G006 and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

W. Si and M. Dudley of SUNY-Stony Brook and T. McClelland of Frequency Electronics Inc. have been investigating processing-induced damage in quartz resonator crystals. Figure 7 is an example of a transmission topograph recorded at X19C from such a resonator showing dislocations, Pendellosung fringes due to the surface contouring, and an increase in fringe density in strained regions resulting from thermal compression bonding.

Figure 7 X19C: White beam transmission topograph ($g=01\bar{1}1$, $\lambda=0.54\text{\AA}$) recorded from a quartz resonator crystal showing dislocations, Pendellosung fringes (labeled P) due to the surface contouring, and an increase in fringe density in strained regions (labeled S) arising from thermal compression bonding. Research funded by Frequency Electronics, Inc.

J. Wu and M. Dudley of SUNY-Stony Brook have been using white beam topography at X19C to investigate the high temperature bending deformation of InSb single crystals. Detailed information regarding relative mobilities of different kinds of dislocations has been revealed.

Monochromatic x-ray transmission topographs of submillimeter high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ twinned and detwinned crystals have been obtained using the X23A3 asymmetric Bragg diffraction microscope, by R. Spal, D. Kaiser, F. Gayle (NIST), and H. Schloessin (UWO). Figure 8(a) is a (200) O-beam topograph of a twinned crystal. The central area is pervaded by intersecting twin lamellae, while the lower right corner is nearly twin free. Figure 8(b) is a (200) O-beam topograph of a thermomechanically detwinned crystal. The strong, rather symmetric, contrast may be due to residual strain from the detwinning process.

Radiographs of strained high- T_c superconductor composite wires, consisting of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ filaments embedded in a Ag matrix, have been obtained using the X23A3 asymmetric Bragg diffraction microscope, by R. Spal, C.K. Chiang (NIST), B. Riley and A. Otto (American Superconductor Corp.). At 0.7% strain, $2\mu\text{m}$ wide cracks in filaments were observed.

Figure 8 X23A3: (200) O-beam topographs of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystals: (a) twinned crystal, $460 \times 235 \times 88\mu\text{m}^3$, (b) detwinned crystal, $340 \times 290 \times 88\mu\text{m}^3$.

David Black from NIST, Stefan Kycia and Alan Goldman from Iowa State University have continued to study the defect microstructure of large single crystals of face centered icosahedral $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ using beamline X23A3. Earlier work [S.W. Kycia et al., *Phys. Rev. B* **48**, 3544, (1993)] showed that these crystals are sufficiently perfect to diffract dynamically. Therefore, transmission images from thick specimens were attempted to record the microstructure within the bulk of the crystals. Figure 9 shows the dislocation structure in a five-fold symmetric transmission image, the (18/29) peak in the indexing scheme of Cahn et al. [*J. Mater. Res.* **1**, 13 (1986)], taken from a sample with a two-fold surface. This image was taken with 19.5 keV x-rays and the diffraction vector is vertical. The central dark region (darker corresponds to increased diffracted intensity) is of high quality and shows individual dislocations. A low angle subgrain boundary is visible running horizontally across the top of the image.

David Black and Harold Burdette of NIST and Nik Buchan and Dave Henshall of Advanced Technology Materials have been studying 6H-SiC single crystals at X23A3. One of the limitations to large area device applications of SiC is a growth defect known as "micro pipes". The micro-pipes are hexagonal voids oriented roughly parallel to [0001], the growth direction. X-ray radiography is an excellent tool to map the size, shape, distribution and morphology of micro-pipes in SiC wafers. Figure 10 shows a radiographic image of part of a 1" diameter x 300 μm thick wafer. The sample was inclined 30 degrees to the beam so the structure of defects which traverse the sample thickness can be observed. The changes in diameter and orientation of the micro-pipes is evident.

Figure 9 X23A3: A (18/29) five-fold symmetric transmission image from a high quality $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ single crystal.

Figure 10 X23A3: An enlargement of the radiographic image of a SiC wafer taken at 8 keV. Darker objects in the image correspond to increased x-ray intensity. Micro-pipes are seen at (1), (2) and (3). The voids at (1) traverse the sample thickness, while the void at (2) is very near the surface. The changes in micro-pipe diameter with growth can be seen at (3).

David Black and Harold Burdette of NIST, Mary Anne Plano of Crystallume and Bill Banholzer from GE Super Abrasives have been investigating the defect microstructure of thick homoepitaxial diamond films grown on isotopically controlled man-made single-crystal substrates at X23A3. Figure 11 shows a (400) symmetric surface image of a substrate prior to deposition. Individual dislocations and stacking faults are visible and the sample shows no inhomogeneous strain. The same substrate is shown in Figure 12 after deposition, also a (400) symmetric surface image. The film has strained the sample and evidence of the substrate defect microstructure is absent. The diagonally oriented structure of the film is due to the surface morphology of the substrate which is visible optically. This surface "relief" is believed to be due to polishing.

Figure 11 X23A3: A (400) symmetric surface image from a man-made diamond substrate.

Figure 12 X23A3: A (400) symmetric surface image after deposition of a homoepitaxial diamond film.

1993 ANNUAL USERS' MEETING

Johnny Kirkland

Naval Research Laboratory / SFA Inc.

NSLS Users' Executive Committee Chairman

The 1993 Annual Users' Meeting and workshops at the National Synchrotron Light Source, held May 19-21, marked the end of another successful year of operation for the VUV and X-Ray Rings. The three day event consisted

with science to the general public, how to discuss the things that excite us in a way that the general public can understand and appreciate. In conclusion, she compared science to a subject that is familiar to all. She stated that

**K.C. Cole (senior editor Discover magazine)
1993 Users' Meeting keynote speaker**

**(left to right): M. Blume (Deputy Dir., BNL);
Tim Elam (NRL);
John Kirkland (UEC Chairman, NRL)**

of five parallel one-day workshops (described later in this issue), a display representing 22 vendors, eleven invited and ninety contributed presentations. The meeting began Thursday morning with a welcome to the attendees by Martin Blume, Deputy Director of Brookhaven National Laboratory. He introduced our keynote speaker, K.C. Cole, who gave an entertaining keynote address.

Ms. Cole is a senior editor for Discover magazine, a self-described voyeur of the sciences. She described what is fun about science and how to look at everyday things in the scientific world, seeing them with a new perspective. She showed us how even relatively simple things such as sine waves and spin are pervasive and connected in our world. K.C. then described how to bring our fascination

science, like sex, has a basic and utilitarian purpose, but that's not necessarily why we do it.

Denis McWhan then gave us an update on how well the NSLS is running and plans for future improvements. Both rings performed very well over the past year with a minimum of unscheduled downtime. Denis then reported on the recent Scientific Advisory Committee (SAC) findings regarding the VUV Ring. The SAC suggested that some PRT's on the VUV Ring be either urged to consolidate their resources with other PRTs, or with the NSLS in return for a higher percentage of general user time. Studies on the X-Ray Ring have been made to see what impact going to a ring energy of 2.8GeV will have on the background radiation. Studies are in progress to inject

and ramp to 500 mA, twice the presently available current as well as to decrease the vertical source size of the ring by a factor of four. Combined with the doubling of current, this improvement would give an eight-fold increase in brightness.

Jon Levin (NIST) next explained his measurements of the double photoionization of helium at high energies. The results, which depend critically on use of single-bunch operations, help elucidate electron-electron correlation in the simplest atomic three-body system. Jon ended his talk by saying that the work wasn't as much fun as sex, but it wasn't a bad way to fool around.

Paul Bertsch (U. of GA) used the microprobe capabilities of X26A to do x-ray microanalysis and

voted upon. Since the charter was the original document for a fledgling organization, changes made were to set the guidelines of the UEC to coincide with the method of operation that had evolved over the years. Everyone adjourned to a delicious lunch under the big top, followed by meetings with the various SPIG's. The following individuals were elected as general members of the UEC: Geraldine Lamble (NCSU/BNL), Paul Lyman (ORNL), and Robert Sweet (BNL).

Gunther Wertheim (AT&T Bell Labs) showed us a wealth of new information that has been obtained by photoemission from the alkali metals. His work makes use of spectra of the shallow np core levels in which the atoms in the bulk and outermost layer yield well-resolved lines.

(left to right): D. McWhan (Chairman, NSLS); M. Dudley (SUNY at Stony Brook)

(left to right): S. Bajt (U. Chicago); L. Yang (APS/ALS)

microspectroscopy to study a range of problems in environmental sciences. The chemical speciation of U in contaminated soils and sediments has been determined *in situ* via spatially resolved XANES where regions of variable oxidation state [U(IV) and U(VI)] could be elucidated and differential bonding environments inferred on a 50 micrometer scale. X-ray microanalysis of groundwater colloids provided direct evidence that the transport of contaminant metals was being facilitated by coassociation with the mobile colloidal phase as trace levels of Cr, Ni, Cu, and Pb, which are signatures of the contaminant source.

Changes to the UEC charter were discussed and

Giovanni Matone (Frascati Inst., Rome) discussed an experiment that is being planned for the LEGS beam line, X5, measuring the polarizability of the pion. The pion is an object with an internal structure of charged objects (quarks); therefore, it can be polarized by electric and magnetic fields. A traditional way to observe the polarizability is to scatter light and observe the deviation from point-like scattering. The polarizability of the pion is of fundamental interest because its value is predicted by an elementary symmetry (chiral symmetry, which is basically just the conservation of helicity). At present, the only measurement is inconsistent with this symmetry. If this value stands, there is something wrong with chiral sym-

metry or the pion is not the carrier of the strong force, either of which goes against everything that has been understood over the past forty years.

Vince Harris (NRL) reported on work using XAFS to detect and measure a structural anisotropy which exists between the in-plane and out-of-plane structure of amorphous Tb-Fe films. These alloys, discovered over 20 years ago, are the mainstay materials of magneto-optic storage devices. The structural anisotropy is described in terms of anisotropic pair correlations where Fe-Fe and Tb-Tb pairs are statistically preferred parallel to the film plane.

At the NSLS/User Community Discussion, 1992-1993 UEC Chairman Neal Shinn (SNL) summarized the progress in improving BNL staff services and housing,

Users' Association presented a gift to Susan White-DePace for her many years of service as the Head of User Administration.

Next morning, Eric Blum (NSLS) described the makeover of the NSLS injection system. Long overdue maintenance, plus hardware upgrades have reduced the time needed for injection for both rings by nearly half. Although most work is finished, there are still some improvements forthcoming.

John Smith (NSLS) discussed the change over of the NSLS computer control system from Data General mainframe and micros using RS-232 communication, to HP workstations using Ethernet. Most of the changes have been made during maintenance and study periods,

(left to right): B. Ocko (BNL-Physics); G. Held (IBM); C. C. Kao (NSLS); K. Hamalainen (U. Helsinki)

(left to right): J. Barkyoumb (Naval Surface Warfare Center); T. Morrison (IIT)

allocation of timing mode operations on the X-Ray Ring, and other user issues. Topics that were brought up for discussion were: space allocation after construction of the new additions, the question of whether to go for increased ring current or increased ring energy on the X-Ray Ring, and noise abatement.

The afternoon concluded with the popular poster session and concurrent social hour at Brookhaven Center. Attendees viewed over 90 posters this year. The conference banquet was held at the Sun Land Manor, which afforded a change of scenery and an opportunity to listen to music provided by a local Renaissance musical group "Measure for Measure." In a brief presentation, the NSLS

with little loss of operations time. The new systems allow much better, faster control of the rings with significantly improved diagnostics.

Charles Meade (Carnegie Inst. of Washington) reported on recent high pressure x-ray diffraction measurements on silica glass and water. These measurements extend the range of pressure for diffraction studies on amorphous materials by more than an order of magnitude, and show that there are dramatic changes in the short and medium range structures of liquids and glasses with compression.

Joseph Hriljac (BNL) covered techniques and applications for high-resolution powder diffraction. A descrip-

tion of the X7A beamline and the use of crystal-analyzer techniques was covered and critiqued. This was followed by a description of the Rietveld procedure for crystal structure refinement.

Larry Carr (Grumman Corp. Research Center) described the pump-probe technique being developed to perform time-resolved spectroscopy in the far IR. Measurements with a time resolution of 1 nsec have been achieved using infrared pulses from beam line U4IR at the NSLS. Time-dependent properties that the far infrared can sense include photoconductivity decay in semiconductors and quasi-particle (broken-pair) relaxation in superconductors. In the future, the ALS could provide pulses for IR spectroscopy on a time scale approaching 10's of psec.

Glenn Held (IBM) concluded the conference with a description of the dynamics of pinned and unpinned steps on vicinal surfaces. Using x-ray scattering and STM he demonstrated that steps on vicinal silver (110) repel each other at all temperatures except in the presence of impurity pinning sites, which induce a phase separation at low temperatures. For vicinal silicon (111) he found that the surface was logarithmically rough at high temperatures, with steps correlated over at least 30000 Ångstroms. The step interactions were well described by a simple model of entropic repulsion.

(left to right): D. Ronglie (Blake Industries); D. Cox (BNL - Physics); P. Coppens (SUNY at Buffalo); R. Harlow (DuPont)

New Scientific Opportunities Using Undulator Radiation from 5 - 30 eV

Steven L. Hulbert , NSLS

The workshop was organized with three goals in mind: (1) description of experiments which require the high flux and high resolution achievable with the U13U undulator source on the NSLS VUV ring, (2) the flux, resolution, polarization, harmonic rejection, spot size, etc. required by these experiments, and (3) description of low energy high resolution beamlines at other facilities.

The workshop began with a description of the U13U undulator source and the proposed 5-30 eV beamline U13UB by Steve Hulbert (NSLS). The U13UB beamline will consist, schematically, of a focusing (and possibly order sorting) optic followed by a long armlength (high resolution) normal incidence monochromator, an optional gas absorption order sorter, and a refocusing optic. An added benefit of this beamline will be that it can serve as an early test-bed for experiments which might be performed at fourth generation sources such as UV-VUV Free Electron Lasers. Erik Johnson (NSLS), provided a summary overview of the NSLS plans for developing such fourth generation sources at BNL.

Biology: John Sutherland (BNL Biology) described five experiments involving biological samples which require the brightness of undulator radiation. These five experiments (Raman scattering, fluorescence/phosphorescence, circular dichroism, and two radiation damage experiments) all require high flux, and their other requirements (photon energy, resolution, polarization, spot size) span the available ranges.

Chemistry: John Hepburn (U. of Waterloo) described three classes of gas phase photochemistry experiments in the 6-30 eV photon energy range which would greatly benefit from the use of undulator radiation: photofragment spectroscopy (pump and probe), photoelectron spectroscopy, and photoionization spectroscopy. These experiments require high flux, high resolution, well-defined polarization, and well-defined timing of the undulator pulses.

Solid State Physics: Eric Jensen (Brandeis U.) described the specific source requirements for high energy resolution photoelectron spectroscopy of solids in the 5-30 eV photon energy range. The widths of excitations in many systems, e.g. superconductor band gaps, phonon energies, semiconductor donor impurity binding energies, surface state peak widths, and some core levels are smaller than can be reasonably measured with laboratory or bending magnet sources. Eric described the flux requirements for angle-integrated and angle-resolved photoemission, and outlined four physical problems which require an undulator source in the 5-30 eV photon energy range.

Kevin Smith (Boston U.) described one class of solid state physics experiments which require the high flux, high photon energy resolution, and tunability of undulator sources in the 5-30 eV range: Fermi surfaces in quasi-low dimensional oxide conductors (transition metal oxide bronzes). Kevin also outlined five future directions for this work, including quasi-two dimensional systems, resistivity transitions, and phonon dynamics.

Cliff Olson (Iowa State U.) described the Iowa State University high-resolution beamline under construction at the Synchrotron Radiation Center (Stoughton, WI). Based on a purpose-built long-period undulator, Cliff's beamline is designed to provide an ideal instrument to do high-resolution angle-resolved photoemission on high- T_c superconductors. In a 17-25 eV primary photon energy

range, this beamline will provide < 5 meV photon energy resolution by a single-reflection normal incidence monochromator, which he will couple with a hemispherical analyzer providing < 5 meV electron energy and 0.5 degree angle resolution.

Peter Johnson (BNL Physics) described the possibility of using high resolution (in photon energy and angle) angle-resolved photoemission to measure the linewidths and lineshapes of quantum well states in metallic thin films at the Fermi level. These systems have the advantage over other systems that these states can be made to cross the Fermi level at normal emission, thereby eliminating broadening due to emission off-normal.

Jim Long (NRL) described angle-resolved photoelectron spectroscopy experiments of laser-excited (pump-probe) solid (semiconductor) surfaces, e.g. the $\bar{X}$ surface state on GaAs(110). The U13UB beamline will provide a factor of 3 - 10 (7-bunch operation) or 10 - 40 (single bunch operation) improvement in count rate for this experiment compared to an x-ray bending magnet. This, combined with elimination of higher harmonic contamination and more efficient electron detection, will enable the measurement, in the laser-excited state, of photosensitive surfaces and bulk carriers.

X-ray Microfocusing Techniques & Applications

Saša Bajt, University of Chicago

Development of x-ray microfocusing techniques has been a very active field in the last few years. With the commissioning of 3rd generation synchrotron sources (ALS, APS and ESRF), where the major advantage over existing synchrotron sources is higher brightness, there is a possibility to make very small beams. Submicron beams might be used to investigate, for example, distributions of trace elements in single crystals, the small-scale structure of genetic material, or defects in microcircuits.

The workshop gave an overview of the current status of different microfocusing techniques in the soft and hard x-ray regions. The aim of the workshop was to bring together experts and potential users of micro-optics from

universities and laboratories world-wide to report about the present status of these techniques and different applications. The very well attended workshop proved to fulfill our expectations.

There were 13 invited speakers. The workshop was divided into two parts: techniques and applications for a) the soft x-ray region, and b) the hard x-ray region. Each part started with an overview talk followed with talks describing some of the techniques in greater detail. The soft x-ray overview talk was given by Shawn Williams (BNL). Ian McNulty (ANL) talked about microfocusing in x-ray holography, which is a promising tool for the high resolution study of microscopic biological and materials science specimens. Erik Anderson (LBL) told us how soft x-ray zone plates are made. x-rays can also be focused using microchannel plates as we found out from Henry Chapman (SUNY at Stony Brook). One of the applications, micro-XANES at the C-edge in proteins, DNA and chromosomes, was discussed by Xiaodong Zhang (SUNY at Stony Brook). Gene Ise (ORNL) gave an overview talk on hard x-rays where he especially compared hard x-ray microprobe methods of 2nd and 3rd generation synchrotron sources. Submicron beams have already been obtained using tapered condensing capillaries. This was the topic of Daniel J. Thiel's (Cornell U.) presentation. Wenbing Yun (ANL) explained how hard x-ray zone plates are lithographically produced. The latest results from the microfocusing beamline at ESRF, which has just begun operations, were reported by Christian Riekel (ESRF). This beamline uses Bragg-Fresnel optics. These optics were also discussed by D. Peter Siddons (NSLS). The last three talks included: a description of the existing microprobe at X26A at the NSLS given by Stephen Sutton (U. of Chicago), covering a great variety of applications done at this unique beamline; predicted microprobe setups for a 3rd generation synchrotron source by Koen Janssens (U. of Antwerp); and microprobe design at the APS by Mark Rivers and Bingxin Yang (U. of Chicago).

At the end of the workshop a bound copy of all transparencies was provided. Many attendants expressed interest in organizing this workshop annually since this field is evolving and spreading so rapidly. I would like to use this opportunity to thank again all the speakers for their contributions.

WORKSHOPS

Scientific Applications of Real Time Computed Tomography (RTCT)

Kelth W. Jones, Department of Applied Science, BNL

Recent developments in synchrotron x-ray sources, x-ray detectors, methods for tomographic reconstructions, development of new approaches to high-speed massively parallel computers and the associated software for visualization of 3-D data sets should make possible the development of x-ray tomographic systems capable of acquiring and displaying 2563 voxels at a rate of 10-15 Hz. The Workshop presentations were intended to give an overview of the ways in which a RTCT instrument could be utilized and to obtain some insights into the problems that would be encountered in its use.

The design ideas for a prototype instrument were presented by BNL-Chicago-Stony Brook scientists to demonstrate the overall feasibility of RTCT. Talks by M.L. Rivers (Chicago), P. Spanne (BNL), W.B. Lindquist (Stony Brook), and A. Kaufman (Stony Brook) covered the system components. A problem associated with the high data acquisition rate is the necessity to rotate the sample at rates up to 300 rpm.

A number of talks on applications of the device for geological studies related to the petroleum industry were given by A. Kantzas (Novacor Research and Technology Corporation), P. Adler (Laboratoire d'Aerothermique), and W. Soll (LANL). They covered both experimental investigations and theoretical modeling of drill core samples and fluid flow.

In the material sciences application areas, talks were given by J. Papazian (Grumman) and H. Herman (Stony Brook). The presentations emphasized the possibility of studying the kinetics of phase transitions in a manner that is not presently feasible. Melting and crystal growth might be suitable subjects. In the case of coating preparation by thermal spray methods it would be possible to study growth of deposited materials and correlate coating morphology (voids, homogeneity, etc.) potential with production conditions. The ability to achieve high frame rates could be exploited for high-speed microscopic projection radiography to determine properties of the plasma particles.

The chemical sciences were covered in talks by A. Kantzas (Novacor Research and Technology Corporation) and W.C. Conner (University of Massachusetts). They covered applications of RTCT in measurements on fluidized bed reactors and the study of various aspects of polyolefin production, respectively. Conner pointed out the desirability of making volumetric measurements of the crystallinity of the polymerization particles, that is, producing images based on intensities of diffracted beams.

R. Avila (Stony Brook) gave a discussion of the state of software methods used in the visualization of biological data. In particular, a video was presented which gave an excellent idea of how the data display would appear to the scientist performing an experiment. Finally, M.E. Coles (Mobil) gave a short summary of the discussions and led a general discussion of RTCT including problems, applications, and directions for future development of the topic.

Recent Advances in XAFS: Techniques and Applications

Lars Furenlid, NSLS

The 65 attendees were treated to talks covering recent experimental applications of x-ray absorption as well as developments in hardware, software and theory.

The morning session was initiated with two talks describing the structural characterization of molecules promoted into excited electronic states by light. James Norris (ANL) opened the workshop with a description of EXAFS measurements of a molecule containing N-O bound to a nickel atom (in a matrix at cryogenic temperatures). Upon photoexcitation, charge is transferred to the ligand from the metal, and the geometry changes from a linear to bent arrangement. The effects on the absorption spectrum, enhanced by the focusing effect associated with linear arrangements, were easily evident. Edward Stern (U. of Washington) discussed a continuous flow technique for EXAFS measurements of excited molecules and the application to Pt "POP", a bimetallic metal-organic complex. Joe Wong (LBL) presented the results of Mg and Si K-shell absorption spectra collected with new YB66 monochromator crystals. The combined advantages of large d-spacing, resistance to radiation damage, and sharp rocking curves make YB66 an attractive choice for 1-2 keV spectroscopy. Lynda Soderholm (ANL) presented results of investigations of metallofullerenes, focusing on the issue of whether metals had indeed been isolated within the carbon cages, as previously claimed. The EXAFS evidence so far suggests that the metals are actually bound externally on these "soccer ball" molecules. In the final talk of the morning session, Ke Zhang (Biostructures Institute) discussed the importance of and techniques for applying a deadtime correction to data collected with energy discriminating solid-state detectors.

The afternoon session was led off with three talks on beamline optics. Peter Eng (U. of Illinois) discussed the design and performance of a new conically bent crystal monochromator. The conical bend permits effective focusing at focal length ratios other than the 3:1 optimal for cylindrical crystals. Gerd Rosenbaum (Biostructures Institute) followed with a description of the sagittal focus-

ing crystal at beamline X9 at the NSLS which uses steel ribbing epoxied to the silicon to prevent anti-clastic bending. The next speaker was Michael Sansone (EXXON Corporation) who presented the mirror feedback system on beamline X10C which keeps the beam's vertical position constant to within a few microns. This dramatically attenuates noise arising from beam motion over sample non-uniformities.

The late afternoon session started with a presentation by Steve Heald (BNL) entitled "A Users Guide to Glancing Angle EXAFS". The talk addressed measurement techniques as well as the fundamental relationships between reflectivity and absorption. The transforms required to map glancing angle data into standard EXAFS were illustrated with studies of structure at interfaces in layered materials. Matt Newville (U. of Washington) was the last featured speaker, describing the theory and applications of new programs based on FEFF, the EXAFS simulation code from John Rehr (U. of Washington) and collaborators. The talk described AUTOBK, an automatic background removal code, and FEFFIT, a multiple scattering fitting code. The sample applications demonstrated the progress being made towards including outer-shell information as a standard part of EXAFS analysis. Data analysis issues were also addressed in the final part of the workshop program. Informal software demonstrations of new data analysis packages were given.

As a whole, the workshop presentations provided ample evidence that x-ray absorption spectroscopy continues to be a strong science at the NSLS, with a steady progression of incremental and innovative developments in beamlines, techniques, and theory.

Towards Short Wavelength Free-Electron Lasers

Ilan Ben-Zvi, NSLS
Herman Winick, SSRL

A workshop dedicated to the establishment of parameters and means for carrying out proof-of-principle Free-Electron Laser (FEL) experiments was held at the NSLS at Brookhaven National Laboratory on May 21-22, 1993.

This workshop was called because of the growing perception in the FEL source community that recent advances have made it possible to extend FEL operation to wavelengths about two orders of magnitude shorter than the 240 nm that has been achieved to date. In addition short wavelength FELs offer the possibilities of extremely high peak power (several gigawatts) and very short pulses (down to 100 fs). Several groups in the USA are developing plans for such short wavelength FEL facilities. However, reviewers of these plans have pointed out that it would be highly desirable to first carry out proof-of-principle experiments at longer wavelengths to gain confidence that the shorter wavelength devices will indeed perform as calculated.

Over 60 scientists from 22 institutions attended this workshop. To get a perspective on future FEL facilities, the workshop opened with a session on Applications and Facility Plans chaired by Martin Blume of BNL. The session began with a talk on applications and technical requirements by Erik Johnson (NSLS). This was followed by presentations of plans for future short wavelength FEL facilities at BNL, Continuous Electron Beam Accelerator Facility, Duke University, Los Alamos National Laboratory, and Stanford Linear Accelerator Center. Following this Andrew Sessler of Lawrence Berkeley Laboratory chaired a panel discussion on Defining Critical Experiments and Their Parameters.

A session on the Availability of Resources, chaired by George Neil of CEBAF, followed. Various groups described existing equipment that could be used to carry out proof-of-principle experiments.

In most cases the equipment located at any single site was inadequate to carry out a full program of proof-of-principle experiments. This led to consideration of

collaborations to collect at one site enough equipment from several sites to minimize the cost of constructing new equipment. This phase of the workshop started as a group discussion, chaired by Brian Newnam of LANL.

Three working groups were established to meet during subsequent sessions to develop experimental programs based on collaborations among the various institutions who could contribute hardware and/or expertise. These groups and their chairmen were: 1) linac-driven amplifiers (both injection-seeded and self amplified spontaneous emission) led by Alan Fisher of BNL and Kwan-Je Kim of LBL, 2) linac driven oscillators led by Charles Brau of Vanderbilt University, and 3) storage-ring driven oscillators/amplifiers chaired by John Madey of Duke University.

Use of Coherent X-Rays for Imaging and Diffraction

Mark Sutton, McGill University

Several experiments at the NSLS are using the high brilliance of the x-ray ring to take advantage of partial coherence. In particular, several groups are using X1 for coherent imaging and several groups are using X25 for coherent diffraction. This Workshop attempted to explain these uses of partial coherence to other interested users of the Light Source and act as a forum for the representatives of the two research areas to get together and explore common themes. The workshop covered how coherence is exploited in several experiments and what new information could be learned. Steve Dierker (U. of MI) introduced the use of coherence in diffraction comparing both light and x-rays. Malcolm Howells (LBL) gave an introductory talk on the formalism of partial coherence and several examples of its use. Brian Stephenson (IBM) discussed the type of information that can be gained by using coherent diffraction to study the kinetics of alloy systems. The final talk was by Steve Lindaas (SUNY at Stony Brook) who discussed the use of coherence in the Scanning Transmission X-ray Microscope and for x-ray Gabor holography.

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2 of 5

VUV MACHINE

Stephen Kramer

VUV Ring Manager

Stephen Kramer, VUV Ring Manager

A detailed breakdown of the VUV Ring performance statistics is shown in the accompanying figures. The most significant increase is in the average charge rate (Figure 2), which after the May shutdown showed marked improvement. This has been largely the result of Eric Blum's dedicated efforts to improve the injection system's reliability, the increase of the linac energy for injection into the booster, and the implementation by Rolf Olsen of a new feed-forward system on the booster dipole power supply. The total integrated current available for users is up only slightly as a result of a change in the fill policy (Figure 3), limiting the injection current to 850 mA, rather than attempting to maximize the integrated current by filling to higher levels. In addition, the four week

spring shut-down reduced the total available operating time to a level comparable to that in FY92. Although a major impact on operating time, this shutdown provided an opportunity to make considerable progress in handling an electrical safety issue in the VUV accelerator systems.

The major improvement in VUV Ring operations has been the completion of the new computer control system. Since March of 1993 the VUV Ring has been controlled entirely by the Hewlett Packard workstations, with the Data General and Vax computers no longer being used. Not only did this eliminate computers that were becoming unreliable and costly to maintain, but it provided the memory and flexibility to provide new control functions and devices. Many of the operator control functions are becoming more automated, freeing the operator to concentrate on understanding the accelerator systems and on improving their operation. The availability of flexible and rapid access to system devices has allowed for the creation of device histories that help to debug changes and glitches in the operation of the ring, not possible with the slower communication systems of the past.

The new control system has made it possible to develop new diagnostic systems and to log their values along with other system parameters. Two new photon beam devices have allowed measurements of changes in photon flux that don't appear to arise from changes in electron beam steering (i.e. not observed by the BPM system or correctable by the Global Orbit Feedback System) and to correlate them with changes in other system parameters. Additional photon beam monitors are planned to help address the issues of beam fluctuations seen by users, that contribute to a non-statistical noise in their data. Improvements in the measurement and control of

the response matrices for the Global Orbit Feedback System (GOFs) have been implemented, improving the orbit stability for all settings of the TOK undulator. The observation of changes in the response matrices and the recommendation of the BPM Design Review have been the driving force for an automated BPM calibration system that can measure and correct for changes in the gain and offset of the BPM receivers. A prototype system is now being tested, and when the entire system is available long-term orbit calibration will be available and verifiable to $<100\text{ }\mu\text{m}$. With the availability of the photon beam position measurements at U14B, the July through September history data shows that the orbit is already resettable to an accuracy of $<300\text{ }\mu\text{m}$ peak-to-peak relative to this monitor at the end of a 7 meter beamline. The U14B monitor also shows that the GOFs maintains a vertical photon beam position stability of $<50\text{ }\mu\text{m}$ peak-to-peak during a fill. Users who require high stability are being advised to consider adding photon position monitors to their beamline, since the control system is already able to monitor additional devices.

Changes made to the VUV Ring operating procedures have helped reduce some of the orbit resettability problems of the past. These changes include a more reliable magnet conditioning cycle and high resolution tune measurements. In the near future, high precision Hall Probes will be installed in the main magnets to help

track and understand changes in their magnetic fields and their impact on orbit changes. To help better diagnose user beam problems, a new User Beam Problem Reporting Form has been instituted. After the user provides sufficient information on the beam problem they observed, the operator on duty will make a preliminary investigation for the cause of the problem and save fast history data to a file before its buffer is overwritten. All filed reports will be addressed by the ring manager and the resolution of the problem reported in writing to the user. As of the end of September no User Beam Problem Reports were filed.

As the fiscal year came to an end the new RF power transmitter for the 4th harmonic cavity was having big success in providing increased lifetime by stretching the bunch length equally for all values of ring current. This not only provided about a 25% increase in integrated current during a fill, but also helped stabilize the longitudinal beam fluctuations in the ring. This resulted from the RF Group taking a conservative approach toward commissioning this system, rather than attempting to achieve maximum lengthening. This system would have been operational in FY93 were it not for an unforeseen signal ground-loop problem which caused the VUV beam to dump when the booster extraction was turned on. This was partly due to an oversight in the distribution of timing signal cables to users. As more diagnostic devices

VUV Ring Performance FY 1993

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.

Figure 7: The VUV Ring current versus time for fills with the 4th harmonic cavity (rf2) :

- tuned (passive bunch lengthening),
- powered for optimum stability and conservative bunch lengthening and
- cavity shorted (shielded from the beam).

The increase in the area for tuned vs. powered cavity is about 25%.

and user signals are provided in the future, improved planning and user cooperation will be required to prevent re-occurrences of these problems. However, by year's end the powered harmonic cavity was already performing so well that the users interested in timing experiments were considering changing their request for detuned 4th harmonic cavity operation in favor of powered harmonic cavity operation. Figure 8 shows the improved lifetime for the powered harmonic cavity operation. Future studies will also attempt to use this cavity for shortening the bunch for timing experiments requiring shorter bunch lengths.

FY94 will continue to see major efforts at improving the beam stability and understanding the sources of orbit drifts. Accelerator studies have already improved our understanding of the impact of nonlinear resonances on the beam lifetime and vertical size. The new control

system and new diagnostic devices will help the physicist to understand the ring model and improve the injection efficiency. Studies have shown a significant increase in beam lifetime with no apparent beam size change at energies up to 825 MeV. Once a new SAR is approved, operations at this or even higher energies could be an advantage to the users. However, the real benefits of these improvements will ultimately be in the science that they will help achieve on the VUV Ring. Improvements in the electron beam properties alone, without similar advances in the photon beamlines, will not maximize the scientific output of this ring. In order to achieve this, we will need to continue to improve in the communications between the users and the NSLS staff so that these ring improvements will be directed toward the most important advances in the photon beam properties needed by the users.

VUV BEAMLINES

Roger Klaffky
VUV Operations Manager

Over the course of FY93 there were 182 different experiments performed, as determined from a count of NSLS safety approval forms. The institutional breakdown of scientists participating in these experiments was 35% from universities, 27% from industry, 18% from BNL, 12% from other DOE labs, 5% from abroad and 3% from government labs.

PRTs and the NSLS made technical improvements on a number of beamlines. Limited operations began on the U2B infrared beamline late in 1992 with the installation of a Nicolet 740 FTIR spectrometer and diamond anvil cell optics. Development work continued on the U3A beamline. Several holographically patterned reflection gratings with multilayer coatings were ordered to provide high resolution. Multilayer analyzers and beryl crystals will also be used in the monochromator. On U4IR a new Michelson interferometer was installed which has a number of desirable features. These include: interchangeable beamsplitters, which will allow the useful spectral range to be extended below 20 cm^{-1} and above 100 cm^{-1} ; a more rapidly scanning mirror for noise reduction, and a more linear scanning system. Plans were made to convert the U5U 6m toroidal grating monochromator to a shorter 3.5m spherical grating monochromator (SGM). The TGM design has several inherent disadvantages when coupled to an undulator source: (1) moderate energy resolution, (2) moderate flux, and (3) a relatively large spot size at the sample. The SGM will increase the photon energy resolving power significantly while simultaneously increasing the flux and decreasing the spot size at the sample from $3\text{mm} \times 2\text{mm}$ to $0.15\text{mm} \times 0.10\text{mm}$. Plans were also made to upgrade the U7A TGM to an SGM in order to increase the photon energy resolving power from 900 to 5000 over a 200-1000 eV energy range. A refocusing mirror placed downstream of the monochromator will decrease the beam dimensions on the sample from $10\text{mm} \times 5\text{mm}$ to $1\text{mm} \times 1\text{mm}$. On U8B a second independent sample handling and introduction system was installed which allows for photomission and allied experiments to be performed on samples at temperatures down to 80K.

On U9B a design for a dedicated fluorometer was completed and orders for all components placed. A position sensitive photomultiplier was acquired which records the time of arrival of a photon in addition to its location on the photocathode. This permits simultaneous measurement of fluorescence decay curves over a broad range of emission wavelengths. An imaging spectrograph was ordered for use with this detector. A SUN SPARC Server 10 was also obtained for archival storage of data generated by the U9B spectrometers and control software was upgraded. A new U11 PRT was formed which will consist of three separate "mini-PRTs": chemistry, biology and solid state physics. The solid state physics mini-PRT made plans to upgrade an NSLS angle-resolved photoemission apparatus to provide ultra-high energy resolution.

The high-energy TGM beamline U12A optical elements were upgraded: a new toroidal front mirror was purchased and the existing monochromator gratings were cleaned and recoated. Both changes should result in an increase of flux delivered to the sample. On the U13UA high flux, high resolution, soft x-ray (100-1200 eV) beamline all three soft x-ray gratings (300, 600 and 1200 line/mm) were installed and commissioned. A 20 degree VUV (30-120eV) extension of U13UA was designed and scheduled for installation in 1994. There were a number of changes to the ultraviolet projection lithography beamline U13UB. In the past, a mirror switcher was used to direct beam into three separate end stations: a 20X reduction Schwarzschild camera for resist evaluation, a 1X Offner ring-field camera for aerial image evaluation and a focalometer for precision metrology of spherical mirrors. All three of these end stations were removed this year and an end station for imaging experiments at 6.8nm wavelength was installed. In the future, end stations for testing complete EUV imaging systems to an accuracy of $\frac{1}{4}$ wave at 14nm wavelength and for carrying out EUV lithography at 14nm will be installed. On U16A the 150mm hemispherical analyzer was remounted on a translation stage to allow for adapting a Mott spin detector to the analyzer system.

VUV STORAGE RING PARAMETERS AS OF MARCH 1994

Normal Operating Energy	0.745 GeV
Maximum Operating Current (multibunch ops.)	1.0 amp (1.1×10^{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
$\lambda_c(E_c)$	25.3 Å (486 eV)
B(ρ)	1.28 Tesla (1.91 meters)
Electron Orbital Period	170.2 nanoseconds
Damping Times	$\tau_x = \tau_y = 17$ msec; $\tau_z = 9$ msec
Touschek Lifetime (dependent on current per bunch and vertical emittance)	200 min @ 200 mA (var. up to 350 min, depending on use of bunch lengthening 211 MHz RF cavity)
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, 1.23
Momentum Compaction	0.023
RF Frequency	52.887 MHz
Radiated Power	14.7 kW/amp of Beam
RF Peak Voltage (typical)	100 kV
Design RF Power	50 kW
Synchrotron Tune (ν_s)	0.002
Natural Energy Spread (σ_e/E)	4.7×10^{-4} , $I < 20$ mA (current and RF voltage dep.)
Natural Bunch Length (2σ)	7.6 cm ($I < 20$ mA)
Number of RF Buckets	9
Typical Bunch Mode	7
Horizontal Damped Emittance (ϵ_x)	1.38×10^{-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 (1 A)	2.3 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
$\alpha_{x,y} = -\beta'_{x,y} / 2$	-0.046 to 1.087, 3.18 to -0.96
$\gamma_{x,y} = (1 + \alpha_{x,y}^2) / \beta_{x,y}$	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

X-RAY MACHINE

Norman Fewell
X-Ray Ring Manager

The overall utilization of the X-Ray Ring for FY93 (Figure 1) closely resembles the excellent performance of the previous year. However, this figure does not reflect the efforts and achievements of the NSLS staff in increasing the potential of the facility while maintaining the scheduled experimental program.

Throughout the year the Computer and Controls Groups have worked vigorously to upgrade the computer control system. In order to maintain the experimental program, the existing multibus micros were systematically replaced by VME micros that could be accessed simultaneously by the existing Data General Eclipse computer

system and by the new HP Workstations via Ethernet. As this conversion progressed the Computer Group modified the programs to work on the new system and also wrote new programs that took advantage of the increased performance of the HP system. These programs were tested out during study periods and soon led to real time orbit measurements and improved orbit correction programs. The Computer Group met its target date of July 17th for complete control of the storage rings by the HP system only and the Data General computers were removed from the building during the following month. The superior capability and speed of the VME system

enabled the replacement of approximately 80 multibus micros by just over 50 VME micros. This reduction in number, plus the fact that they have battery backed-up memory, will lead to increased reliability. Furthermore, the speed of the system will result in improved diagnostic and performance capabilities. With the new control system in place the Computer Group can now concentrate on new programs that speed up the availability of beam to the users and also provide information on the beam position, stability, etc.

The installation of a fourth 52 Mhz RF system during the 1992 fall shutdown was the result of a concerted effort by the Mechanical, Vacuum, and RF Groups. This installation makes available a significant increase in the X-Ray Ring's performance and allows repair of a system while operating at the present current of 250 mA at 2.58 GeV. Due to a reduction of one fourth in the acceleration voltage required from each cavity, the RF power with four systems is sufficient to double the stored beam from 250 mA to 500 mA at 2.5 GeV. Study periods have been used throughout the year to reach this design limit, which was successfully accomplished on Sept 30, 1993. The Mechanical and RF Groups built two new RF transmitters to

Norman Fewell, X-Ray Ring Manager

replace the existing ones in systems 1 and 2. These new transmitters, which will be installed during the 1993 fall shutdown, use Eimac Y567 electron tubes which are more robust than the present tubes used in the system. Their longer operational life time and higher power capability should result in a more reliable system. Operations, however, will continue at a current limit of 250 mA due to thermal limitations of the insertion devices' vacuum chambers. A task force headed by Lonny Berman is now studying the thermal limits of these chambers to determine whether they can be upgraded to meet the new beam performance of the X-Ray Ring. In the meantime studies have continued at 350 and 380 mA with the insertion devices open (X17 off) to allow bending magnet beam lines to study the heating effects of high current levels on their optics. These studies will continue with beam currents up to the design limit of 438 mA at 2.584 GeV.

Studies have also been done at low current with the energy increased to 2.8 GeV to evaluate the adequacy of the beamline shielding. Measurements so far indicate an increase of approximately seven times the existing beamline scattering radiation levels. These studies will continue at low current levels until the beamline radiation surveys are complete.

The 1992 fall shutdown was also utilized to install new power supplies for the booster to X-Ray transport line magnets and to install additional skew quadrupoles in the X-Ray Ring. The skew quadrupole installation makes possible adjustment of the electron beam's horizontal to vertical coupling. This coupling is caused by imperfect magnet fields or magnet alignment errors and transfers some horizontal beam motion into vertical motion, thereby

increasing the vertical beam size. During studies James Safranek (NSLS) demonstrated that by using the skew quadrupoles the vertical beam size can be reduced by a factor of two. This reduction in vertical beam size, however, results in a slight reduction in beam lifetime due to electron/electron scattering (Touschek effect). Fills with reduced vertical size are being made to enable the users to decide when operational periods utilizing this achievement should be put into effect.

Work by Om Singh and the Controls Group has improved the local and global beam position feedbacks by decoupling the systems. Due to limited space for correction magnets and position monitors in the X-Ray Ring, the actions of local and global feedback systems overlap. Local orbit corrections could couple to the global system and produce orbit movement around the ring. Conversely the global system could act to inhibit the local correction. Om has successfully devised circuitry that decouples the systems, resulting in improved orbit stability and less likelihood of oscillation and lockup due to magnet glitches.

X-Ray Ring integrated current (Amp Hours) is shown in Figure 2. This figure, however, is no longer a measure of the X-Ray Ring reliability and performance, but rather an indication of the various scheduled user beam parameter requirements. The integrated current per month now depends upon the X5 experiment and timing runs with five or single bunches. The fall shutdown is obvious in the figure, but the reduced value for July is the result of five days of five bunch operation and six days of single bunch operation, and April includes two weeks of shutdown and two weeks of five and single bunch running.

Figure 1: The breakdown of the X-Ray Ring usage based on total time (not scheduled time) for FY93.

Figure 2: The total integrated current for the X-Ray Ring accumulated each month for FY93.

X-RAY BEAMLINES

Roger Klaffky
X-Ray Operations Manager

During FY93 there were 920 different experiments performed, of duration several days to six months, as determined from a count of NSLS Safety Approval Forms. The institutional breakdown of scientists participating in these experiments was 43% from universities, 19% from industry, 15% from BNL, 10% from other DOE laboratories, 8% from abroad and 5% from government labs.

PRTs and the NSLS made a substantial number of beamline technical improvements. On X1A a new VAX 4000 work station with IDL based software to run the scanning transmission microscope was installed. Upgraded vibration isolation was provided for the microscope optical bench. A new photoelectron microscopy chamber and electron analyzer were also assembled. The X1B vertical focussing mirror was replaced by a new mirror manufactured from silicon, which has better thermal characteristics. The mirror has produced an improved focussed image at the entrance slit with an associated increase in flux. The X2A beamline design was completed and purchase orders placed for major components. On X2B a new CCD detector configuration was developed for installation in 1994. On X3A1 new image plate techniques were implemented and a radiation shield to remove parasitic scattering was mounted inside the Displex cryostat. New high-speed, high-torque motors with 0.001° angular steps were installed on the X3A2 diffractometer to provide improved phase determination in protein crystallography experiments. The X3B1 station was upgraded to provide a general purpose powder diffraction capability. Improvements to the monochromator allow continuous tuning from 5 to 40 KeV [with Si(111) crystals]. A diffractometer in the hutch spans 110° in 2θ , and accommodates environmental chambers for sample heating and cooling. The X6A energy dispersive x-ray absorption spectroscopy beamline began operations in 1993. On X7A a VAX 4000 workstation was installed for faster data processing. On X7B testing of a high-resolution ccd detector was carried out, indicating that powder diffraction profiles can be sampled at intervals as fine as 0.0025° providing for reliable integrated intensity measurements on peaks as narrow as 0.01° . A new end station for high accuracy UHV mirror (and crystal) reflectivity measure-

ments was commissioned on X8A. A water-cooled aperture assembly was installed and monochromator analyzer pairs of metal multilayers and beryl were replaced improving performance from 300 eV to 2100 eV. A hutch was constructed for the future X9A doubly-focussing beamline. The downstream section of X11B was redesigned to optimize for low energy XAFS data collection. The section includes a thin Be window, a feedback system, a double-bounce harmonic rejection mirror system and horizontal and vertical slits. A configurable collimator array was completed on X12B. There were upgrades in the sample changer electronics and software and in the data readout system of the 2D real-time gas detector system. A helium glove box sample handler facility was also completed. On X12C the addition of a beryllium window, and new valves and pumps enhanced the storing vacuum protection and provided for independent pumping of each beamline section. The NSLS replaced the monochromator drive with an external screw and bellows feed-through in order to improve reliability and resolution.

The X15A computer control/data acquisition system was upgraded to a 486 PC/CAMAC system running SPEC. The installation of an in-vacuum PIN diode x-ray reflectivity detector increased the maximum 2θ angle from 30° to 170° . The θ - χ diffractometer was replaced with a z - x - 2θ - χ diffractometer making it possible to do total external reflection x-ray standing wave measurements and x-ray reflectivity measurements of thin-film overlayer structures, as well as high precision x-ray optical experiments. A new mirror with an rms roughness of 5 Å and an rms slope error at 3×10^{-6} radians was installed on X16A leading to a factor of two decrease in the vertical spot size and better than a factor of four decrease in the horizontal spot size. A new surface diffractometer was installed with an enhanced specular rod reflectivity range and the ability to deposit material while performing x-ray diffraction.

A tunable monochromator, providing photons up to 90 KeV with Si(220) crystals in a Laue-Laue arrangement, was installed and commissioned on X17B1. A new 1200 element, 0.25mm horizontal resolution, dual-beam detector and associated electronics were installed and used

to image patients on X17B2. Also, upgrades were under development for the monochromator, patient chair, detector, shielded hutch, beamline components (beam attenuators, support structures, monitors), personnel protection system and imaging workstation. These upgrades are part of the twelve month Coronary Angiography Reliability Upgrade project.

On the X18A beamline the addition of an external rough adjustment capability for the crystal provided for less beamline downtime due to vacuum chamber vents. Also the mounting of a horizontal scanning stage on the 2- θ arm allowed for more flexibility in surface diffraction experiments.

A laser alignment system was designed and implemented on X19A which permits the rapid and accurate positioning of all detectors and samples on the x-ray beam axis. In addition, preparations were made for the final installation of the beamline collimating mirror and thin window system. On X19C a horizontally scattering Si(111) monochromator was installed. Improvements to the X20 beamlines in 1993 included updated computer control/data acquisition programs, installation of a new X20C monochromator chamber and a change in the monochromator crystal offset to obtain lower x-ray energies, and installation of kinematic pads in the X20A hutch floor. A water-cooled horizontally focussing Si(220) monochromator and a spherically-bent Si(444) analyzer were commissioned on X21.

Fabrication of the X22A hutch was completed, electrical and plumbing systems were installed as well as all vacuum hardware and pumps upstream of the monochromator. Improved resolution and harmonic rejection were achieved on X23A2 with a changeover from Si(220) to Si(311) monochromator crystals. On X23A3 all hutch

SAXS, and topography imaging equipment was replaced and software was upgraded. The X24A beamline's low-energy range was extended to <1800 eV at high resolution by using the mismatched crystal pair InSb/KDP in the double-crystal monochromator. A heat pipe was developed for alkali metal atoms to extend x-ray photoabsorption measurements beyond the rare gases. Hard limit switches

Roger Klaffky, Beamline Operations Manager

were installed in the X24A monochromator and interfaced to electronics that enable the monochromator to be controlled by general user data acquisition computers and software. W-Be multilayer mirror flats were installed on X24C to provide high flux in the 200-1500 eV energy range with low resolution (3% bandpass).

On X25 a smoother platinum-coated silicon mirror replaced the original one, and a meridional first crystal bender, to compensate for thermal distortion, was installed in the monochromator. The new mirror reflects the same power as the old one, but has a 20% smaller focal

spot size in both the horizontal and vertical. With optimization of the first crystal bender, a monochromatic flux gain of up to 40% using Si(111) at 8 keV was realized, accompanied by a more stable focal spot dimension with changing current, in comparison with the old floating monochromator first crystal. Additional shielding in the monochromator tank to dump the unused incident white beam power and restrict superfluous scattered x-ray power from the mirror and first monochromator crystal resulted in significantly improved monochromator stability.

Instrumentation innovations on X26A included the successful use of a microbeam produced by a 1.3 micron tapered glass capillary for trace element spot analyses and 2D element mapping. Also, a new 13 element Ge detector was implemented which is capable of full fluorescence spectral acquisition from each crystal. To create space for end stations on U13UA, the X27 hutch was moved 1 m upstream and the X28A/C hutch was rebuilt with a 1 m decrease in length. All X28A,B, and C beamline pipes and safety systems were re-installed.

X-RAY STORAGE RING PARAMETERS AS OF MARCH 1994

Normal Operating Energy	2.584 GeV
Maximum Operating Current	0.25 amp (10^{12} e ⁻)
Lifetime	~20 hours
Circumference	170.1 meters
Number of Beam Ports of Dipoles	30
Number of Insertion Devices	5
Maximum Length of Insertion Devices	< 4.50 meters
$\lambda_c(E_c)$ at 1.22 T (B)	2.48 Å (5 keV)
$\lambda_c(E_c)$ at 5.0 T (W)	0.60 Å (20.8 keV)
B(ρ)	1.22 Tesla (6.875 meters)
Electron Orbital Period	567.7 nanoseconds
Damping Times (2.5 GeV)	$\tau_x = \tau_y = 6$ msec; $\tau_z = 3$ msec
Touschek (2.5 GeV, 0.25A)	≥ 16 hrs ($v_{RF} = 700$ kV)
Lattice Structure (Chasman-Green)	Separated Function, Quad Triplets
Number of Superperiods	8
Magnet Complement	<div style="display: flex; align-items: center;"> <div style="font-size: 3em; margin-right: 10px;">{</div> <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> </div>
32 Sextupole	(0.20 meters each)
Nominal Tunes (ν_x, ν_y)	9.15, 6.20
Momentum Compaction	0.0065
R.F. Frequency	52.88 MHz
Radiated Power for Bending Magnets	126 kW/0.25 amp of Beam
R.F. Peak Voltage	700 kV
Design R.F. Power	300 kW
ν_s (Synchrotron tune)	0.002
Natural Energy Spread (σ_e/E)	8.2×10^{-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)	1.1×10^{-9} meter-radian
Power per Horizontal milliradian (0.25A)	20 watts

Arc Source Parameters

Betatron function (β_x, β_y)	1.09 to 2.96 m, 9.54 to 18.53 m
Dispersion function (η_x, η_y)	0.420 to 0.007 m, -0.351 to 0.175 m
$\alpha_{xy} = -\beta'_{xy}/2$	-0.199 to 1.357, -2.18 to 2.19
$\gamma_{xy} = (1 + \alpha_{xy}^2)/\beta_{xy}$	0.952 to 0.962 m ⁻¹ , 0.532 to 0.291 m ⁻¹
Source size (σ_x, σ_y)	371 to 565 μ m, 102 to 143 μ m
Source divergence (σ_x, σ_y)	439 to 324 μ rad, 24 to 10 μ rad

Insertion Device Parameters

Betatron function (β_x, β_y)	1.60 m, 0.435 m
Source divergence (σ_x, σ_y)	260 μ rad, 50 μ rad

PLANS FOR A DUV-FEL FACILITY AT THE NSLS

Ilan Ben-Zvi
Erik Johnson
Sam Krinsky
Li-Hua Yu

The NSLS department has recently completed a design for a Deep Ultra-Violet Free Electron Laser (DUV-FEL) facility, described in a detailed Conceptual Design Report.⁽¹⁾ This DUV source is characterized by a high peak power in the GW range, 10^{-4} bandwidth, pulse repetition rate of up to 360 Hz, a wavelength range from 300 nm to 75 nm and picosecond to sub-picosecond pulse duration. This fourth generation light source will make possible new avenues of inquiry in time resolved studies in diverse fields including chemical, surface and solid state physics, biology and material science.

A unique opportunity to make an early entry into the fourth generation source arena at a modest investment is presented by the availability of the 200 MeV linac from the SXLS project. Figure 1 shows the proposed facility in

an extension of building 729, opposite the NSLS on Railroad Street. To produce the UV radiation, a pulsed electron beam is first generated in a high-brightness laser-photocathode RF gun and accelerated by an in-line single pass S-band linear accelerator. The electron bunch enters a superconducting undulator in phase with a 'seed' laser pulse which is generated by a 'conventional' tunable Ti-sapphire laser followed by a conventional solid-state frequency multiplication stage to produce seed radiation in the visible or near UV. In the first (or modulator) section of the undulator, the electric field of the seed radiation interacts with the electrons in a resonant process to produce an energy modulation in the electron beam. The energy modulation in the electron beam is then converted to spatial modulation in a dispersive magnet. This spatial modulation has a strong harmonic content. This at-

Figure 1: The layout of the proposed BNL DUV-FEL facility.

tribute is exploited in the next section of the undulator, known as the radiator, which is resonant to an harmonic of the seed wavelength. When the coherently bunched beam enters the radiator section, there is a rapid coherent generation of radiation at the harmonic wavelength within the first meter where the radiation has a characteristic quadratic dependence on the distance traversed in the undulator. There is then a transition to exponential growth which continues to saturation some distance into the undulator. To extract further energy from the beam, the field in the remaining length of the undulator is tapered to account for the energy loss in the electron beam and maintain resonance.

The VUV wavelength is tuned by synchronously varying the seed laser wavelength and the energy of the electron beam to maintain the FEL resonance condition. This approach has several advantages over the more conventional method of tuning by changing the undulator gap, including:

1. Simplified undulator design;
2. Undulator operation at maximum field;
3. Rapid wavelength tuning, limited in principle only by the seed laser tuning speed.

To succeed in producing coherent radiation at such short wavelengths, an extremely low emittance electron beam must be generated, transported, and accelerated without degradation. For this cornerstone technology, we rely upon a laser-photocathode RF gun of the type that has been developed at the Accelerator Test Facility (ATF). A high repetition rate RF gun has been designed in collaboration with Grumman Aerospace Corporation. The gun will operate at the linac's repetition rate of 360 Hz and deliver electron pulses ten pico-seconds long with a charge of about 4 nC per pulse. Extensive simulations of the gun's performance lead us to anticipate a normalized rms emittance of about 4π mm-mrad, a value that is similar to that achieved at the ATF.

The undulator design will be based on the superconducting undulator that has been developed at the ATF for a visible FEL oscillator experiment. This undulator has a high axial magnetic field, high precision, and low cost per unit length. Another superconducting undulator is being developed for the High Gain Harmonic Generation experiment on the ATF. In this experiment, a CO₂ laser with about 1 MW input power will be used to bunch a 30 MeV electron beam. Several important features of the FEL will be studied including the super-radiant growth of the third harmonic at a wavelength of 3.47 μ , amplification in the exponential growth regime, and finally the characteristics of amplification in a tapered wiggler sec-

tion. The results of these experiments will provide important tests of the theoretical models of the harmonic generation and gain processes, and answer important questions such as the effect of electron beam parameters on the coherence of the FEL, the effect of wiggler and alignment errors, and the higher harmonic contents of the FEL output as a function of the level of saturation. This experiment will serve in a number of ways as proof-of-principle for the DUV-FEL facility.

Unlike FEL oscillators requiring cavities, the seeded beam FEL amplifier approach is a single pass device, eliminating the resonator and outcoupler mirrors which are a difficult aspect of oscillator FEL designs. An FEL utilizing the harmonic generation and laser amplifier scheme described here provides a source of high peak power VUV radiation with the mode structure, bandwidth, and frequency stability of the input seed laser. In this regard, it is important to note that the FEL is essentially a high quality amplifier and harmonic generation device for conventional solid state laser systems. This feature suggests that many areas of current interest in laser technology can be extended with the DUV-FEL.

For example, chirped pulse amplification (CPA) has been utilized to produce extremely short pulses (50 fs). However, because of the properties of the gain media, amplification of the short pulses is difficult, and operation at wavelengths below about 180 nm is impossible. The DUV-FEL can overcome these limitations, and an experiment has recently been proposed that would produce 3 fs pulses of 88 nm radiation with peak power exceeding 100 GW!⁽²⁾ Similarly, the promise of recent work in coherent control of quantum dynamics utilizing shaped pulses from solid-state lasers is directly transferable to the DUV-FEL.⁽³⁾ These properties will be invaluable to the investigators proposing to use the radiation from the DUV-FEL for experiments in chemical dynamics, photo-biology, and solid state physics.

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NSLS BUILDING EXPANSIONS

Bill Foyt
NSLS

THE ACCELERATOR TEST FACILITY (ATF)

Ilan Ben-Zvi
Ken Batchelor

Free-Electron Lasers (FEL) are considered by many to be the fourth generation synchrotron light sources. The NSLS is carrying out an extensive R&D program on short wavelength FELs, leading toward a proposal for a DUV-FEL Facility⁽¹⁾. The Accelerator Test Facility⁽²⁾ (ATF) is a linac-laser complex capable of producing high brightness electron beams and high power laser pulses synchronized with the electrons. The ATF is the test bed for developing and testing the components needed for a successful UV FEL. At the same time the ATF is serving an advanced accelerator R&D program such as laser acceleration of electron beams and the interaction of intense laser pulses with high brightness electron beams.

The ATF is operated as a users' facility for accelerator and beam physicists. The high brightness electron beam of the ATF, produced by a laser-photocathode RF gun⁽³⁾, has been available for experiments and the overall stability of the laser improved considerably during this year. At present, three experiments are in progress, a Smith-Purcell experiment run by a Dartmouth - MIT - BNL team, an Inverse Cerenkov accelerator experiment by STI Optronics and a visible FEL experiment using a pulsed wiggler developed by MIT.

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 is an area of intense activity in accelerator physics, being the key to short wavelength FELs. As a result of the high performance of this BNL gun, this design has been adopted by numerous laboratories in the USA, Europe (e.g. CERN) and Japan. A new magnesium photocathode which shows promise of an order-of-magnitude greater quantum efficiency has undergone preliminary tests with encouraging results.

The other key components of the BNL ATF are a 50 MeV (up to 100 MeV in the future) electron linac, a 10 ps, 10 mJ Nd:YAG laser, a 20 GW CO₂ laser system producing 50 ps pulses. The lasers are synchronized to within one picosecond to the electron beam pulses. Dur-

ing 1993 the construction of the linac systems, beam transport and beam line #3 in the experiment hall has been finished and the lasers and 50 MeV beams tested in the experiment hall to the beam stops in both line #1 and line #3.

ATF experiments with a special interest for the NSLS short wavelength FEL programs are the RF gun development program, the visible wavelength FEL oscillator experiment and the high-gain harmonic-generation experiment. The FEL experiments also include the development of novel superconducting undulators providing a high field and very low magnetic field error.

The RF gun program produced the now famous "BNL gun" model, a one-and-a-half cell π mode S band gun, operating at a peak cathode electric field of 100 MV/m. However, our program has gone beyond that. An extremely fruitful collaboration has been established with Grumman Aerospace Corporation in which a potentially higher brightness and, most importantly, a very high duty factor gun has been developed and is now in an advanced production stage⁽⁴⁾. To carry out this program, Grumman has invested a significant amount of their internal R&D funding. The gun will be tested at the ATF. A second one-and-a-half cell gun has been fabricated and is undergoing RF testing. It will be used in-line with the linac and, through the use of a solenoidal focussing system, is expected to provide at the exit of the linac a normalized transverse emittance with most of the space-charge-induced distortions corrected.

The visible FEL oscillator⁽⁵⁾ will employ 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). Prototypes of this undulator (up to 23 periods long) were built and performed extremely well in superconducting tests⁽⁶⁾. 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. Emittance scales with energy so that at 250 MeV a wavelength of 100 nm would be practical.

At present, the visible FEL oscillator beam line has another undulator in position. This undulator, developed by MIT, is a pulsed device. Its parameters are 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.

The high-gain harmonic-generation experiment⁽⁷⁾ is another facet of the technology-transfer collaboration with Grumman, which is providing 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 focussing 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 User Facility UV 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.

Other light source techniques are being pursued at the ATF. A final example is the coherent synchrotron emission experiment, in which the short, high charge ATF pulse will generate coherent and intense mm wave radiation in a bending magnet. This radiation will also be used as a pulse length diagnostic for the ATF.

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NSLS ADVISORY COMMITTEES

1993-1994

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: Johnny Kirkland, Naval Research Lab/SFA, Inc.

Vice-Chairperson: Jean Jordan-Sweet, IBM

Secretary: Paul Lyman, Northwestern U.

Alastair MacDowell, AT&T

Robert Sweet, BNL Biology

Chris Jacobsen, SUNY-Stony Brook

Geraldine Lamble, NSLS/NCSU

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	Jon Levin, NIST
Energy Dispersive Diffraction	Syed Qadri, Naval Research Lab/SFA, Inc.
Lithography, Microscopy,	
Tomography, X-Ray Fluorescence	Sasa Bajt, U. of Chicago
Nuclear Physics	Craig Thorn, BNL Physics
Students and Post Docs	Carol Hirschmugl, NSLS
Time Resolved Spectroscopy	James Long, Naval Research Lab
Topography	Michael Dudley, SUNY-Stony Brook
UV Photoemission, Surface Science	David Heskett, U. of Rhode Island
XAFS	Geraldine Lamble, NSLS
X-Ray Scattering, Crystallography	Randy Alkire, ANL

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 and September of 1993 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 1992, March 1993, and July 1993 to review and rate General User research proposals for the FY93 cycles. PSP members are drawn from the scientific community and usually serve a two year term. Members during FY93 were:

UV Panel

Dan Fischer	Exxon
Chi-Chang Kao	NSLS
Dawn Laplano Smith	IBM
Gunther Wertheim	AT&T
Roger Stockbauer	Louisiana State U.
John Sutherland	BNL Biology

X-Ray Imaging/Other Panel

Denny Mills,	ANL
Brian Tonner	U. of Wisconsin
Per Spanne	BNL DAS
Chris Jacobsen	SUNY @ Stony Brook
Ed Westbrook	ANL
Paul Cowan	ANL

X-Ray Spectroscopy Panel

Joseph Budnick	U. Connecticut
Slade Cargill	IBM
Timothy Haye	RPI
Bruce Gates	U. of Delaware
Gerry Huffman	U. of Kentucky
Mark Antonio	ANL
Ronald Felton	Georgia Inst. of Tech.

X-Ray Scattering Panel

Richard Harlow	DuPont
Quintin Johnson	Materials Data, Inc.
David Sayre	self employed
Peter Eng	AT&T Bell Laboratories
Glen Held	IBM

General User Oversight Committee

The General User Oversight Committee (GUOC) met in November 1992, March 1993, and July 1993 to allocate time on beamlines to each General User proposal for the FY93 cycles. GUOC members are drawn from the scientific community and usually serve a two year term. Members during FY93 were:

UV Members

Jan Hrbek	BNL Chemistry
Larry Carr	Grumman
Kaldee Lee	SUNY @ Stony Brook
Roger Bartlett	LANL
C.T. Chen	AT&T
Paul Stevens	Exxon

X-Ray Members

Jean Jordan-Sweet	IBM
Paul Zschack	ORNL
Lars Furenli	NSLS
Gerry Labmlie	N. Carolina State U.
Sean Brennan	SSRL
Fulong Lu	U. of Kentucky
Peter Stephens	SUNY @ Stony Brook

NSLS STAFF

NSLS STAFF

* Temporary

** Reports to John Axe,
Assoc. Dir. for Basic Energy Sciences

() PRT personnel or member of non-NSLS division

(signed) **Denis McWhan, Chairman**

October 1, 1993

NSLS BEAMLINE GUIDE

APRIL 1993

This table lists the abbreviations appearing in the Beamline Guides. Where a four-digit telephone extension is given, it should be dialed as (516) 282-xxxx from outside BNL.

ARUPS	=	Angle-Resolved Ultraviolet Photoemission Spectroscopy
CD	=	Circular Diachroism
C-T	=	Czerney-Turner
ERG	=	Extended Range Grasshopper
EXAFS	=	Extended X-ray Absorption Fine Structure
IR	=	Infrared
LEGS	=	Laser Electron Gamma Source
MCD	=	Magnetic CD
MI	=	Michelson Interferometer
NEXAFS	=	Near Edge X-ray Absorption Fine Structure
NIM	=	Normal Incidence Monochromator
PGM	=	Plane Grating Monochromator
SEXAFS	=	Surface EXAFS
SGM	=	Spherical Grating Monochromator
S-N	=	Seya-Namioka
SXES	=	Soft X-ray Emission Spectroscopy
TGM	=	Toroidal Grating Monochromator
TOK	=	Transverse Optical Klystron
UPS	=	Ultraviolet Photoemission Spectroscopy
WB	=	White Beam
XPS	=	X-ray Photoemission Spectroscopy
XAS	=	X-ray Absorption Spectroscopy

VUV BEAMLINE GUIDE

Beam line	Research Program	Mono.	Affiliation	Local Contact	Spokesperson
U1A	SEXAFS, ARUPS, XPS	ERG	Exxon	B DeVries 5206 908-730-3032	P Stevens 4828 908-730-2584
U1B	(Conceptual)	TGM	Exxon	B DeVries 5206 908-730-3032	P Stevens 4828 908-730-2584
U2A	(Unassigned)				
U2B	High pressure, pump-probe, high Tc absorption	MI	SUNY@SB BNL-NSLS Grumman Carnegie Inst of Was	G Williams 7529 516-282-7529	G Carr 5502 516-346-9073
U3A	Time-resolved and DC radiometry; reflectometry for optical constants	ERG	Los Alamos Natl Lab Smiths Astro Obs EG&G Energy Meas	W Towell 5521 516-282-7245	R Blake 5521 505-983-9683
U3B	(Conceptual)				
U3C	Photoelectron spect.; exp. system and detector calibrations	ERG	Los Alamos Natl Lab Sandia Natl Lab	A Andrews 4751 516-282-5503	A Arko 505-665-0758 R Bartlett 505-667-5923
U4A	ARUPS of solids, surfaces; hi res. core level photo-emission; total yield absorption	TGM	ATT U of Oregon	M Shek 5930 516-282-5930 J Rowe 908-582-5878	G Wertheim 908-582-4958
U4B	Soft x-ray photoemission spectroscopy; NEXAFS; SXMCD	SGM	ATT	G Meigs 7290 908-582-3863	C Chen 7290 908-582-6030
U4IR	Vibr. spectr of molecules on surfaces; abs of hi Tc superconductors; hi res gas abs.; fast detectors	MI	BNL-NSLS ATT Fairleigh Dickinson Exxon	C Hirschmugl 7253 516-282-7253	G Williams 7529 516-282-7529

Beam line	Research Program	Mono.	Affiliation	Local Contact	Spokesperson
U5	Diagnostics		BNL-NSLS	R Nawrocky 4449 516-282-4449	R Nawrocky 4449 516-282-4449
U5U	Spin polarized angle- resolved ultraviolet photoemission	TGM	BNL-Physics	S Hulbert 7570 516-282-7570	P Johnson 516-282-3705
U6	Lithography	WB	IBM	J Silverman 914-945-2099	J Silverman 914-945-2099
U7A	Photoemission; SEXAFS	TGM	BNL-NSLS BNL-Physics	Q Dong 5507 515-282-5505	S Hulbert 7570 516-282-7570
U7B	Photoemission; SEXAFS	PGM	BNL-Physics SUNY@SB	F Loeb 2092 516-282-2092 M Ruckman 3515 516-282-3515	M Strongin 3763 516-282-3763
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				
U9B	CD; MCD; time-resolved fluorescence (lifetimes)	C-T	BNL-NSLS BNL-Biology	J Sutherland 3279 516-282-3406	J Sutherland 3279 516-282-3406
U10A	(Unassigned)				
U10B	PSD - general vacuum R&D	WB	BNL-NSLS LLNL	C Foerster 4754 516-282-4754	C Foerster 4754 516-282-4754

Beam line	Research Program	Mono.	Affiliation	Local Contact	Spokesperson
U11	Gas phase photoionization	NIM	BNL-NSLS BNL-Chemistry U of New Mexico BNL-DAS	L Kelly 2091 516-282-2091 S Kuo 7003 516-282-7003	R Klemm 4022 516-282-4001
U12A	High resolution core level spectroscopy	TGM	Oak Ridge Natl Lab U of Tennessee	D Zehner 5512 615-574-6291	E Plummer 615-974-2288 D Zehner 615-574-6291
U12B	Angle-resolved photoemission	TGM	Oak Ridge Natl Lab U of Tennessee	D Zehner 5512 615-574-6291	D Zehner 5512 615-574-6291
U13UA	High resolution VUV/soft x-ray scattering; electron and ion spectroscopies	SGM	BNL-NSLS Drexel U U of Wisconsin Brandeis U Rutgers U ATT	S Hulbert 7570 516-282-7570	S Hulbert 7570 516-282-7570 E Jensen 617-736-2865
U13UB	Optical metrology for soft x-ray projection lithography	WB	ATT Sandia Natl Lab	A MacDowell 5334 516-282-5334	R Freeman 908-949-9500
U14A	Solid state photoemissions studies	PGM	BNL-NSLS	M Shek 5930 516-282-5930	M Shek 5930 516-282-5930
U14B	Detector Research and Development	WB	BNL-NSLS	J Hastings 3930 516-282-3930	J Hastings 3930 516-282-3930
U15	Soft x-ray spectroscopy (solids and gases)	TGM	BNL-NSLS SUNY@SB SUNY@Buff	D Ji 5515 516-632-7918	D Hanson 516-632-7917
U16A	(Unassigned)				
U16B	ARUPS; XPS; SEXAFS; stimulated desorption; NEXAFS	ERG	Cornell U Sandia Natl Lab	S Woronick 5516 516-282-5516	R Merrill 607-255-9857

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 IBM LBL	S Wirick 4723 516-632-8095	J Kirz 4723 516-632-8106
X1B	Soft x-ray spectroscopy	10-50 Å	BNL-NSLS BNL-Physics FA - Juelich Fritz-Haber-Inst	P Johnson 516-282-3705	P Johnson 516-282-3705
X2A	Small angle scattering		Exxon	K Mohanty 5644 516-282-5644	D Noh 908-730-2548
X2B	X-ray microtomography	6.5-30, WB	Exxon	K Mohanty 5644 516-282-5644	D Noh 908-730-2548
X3A1	Short wavelength crystallography, diffraction and scattering	18.2, 29.7	SUNY@SB SUNY@Buff	A Darovsky 3770 516-282-3770	P Coppens 716-829-3911
X3A2	Diffraction; x-ray spectroscopy; scattering; crystallography; small angle scattering	4-34	SUNY@SB SUNY@Buff	A Darovsky 3770 516-282-3770	P Coppens 716-829-3911
X3B1	X-ray spectroscopy; powder diffraction	4-40	SUNY@SB SUNY@Buff	A Darovsky 3770 516-282-3770	P Coppens 716-829-3911
X3B2	Surface science	4-20	SUNY@SB SUNY@Buff	A Darovsky 3770 516-282-3770	P Coppens 716-829-3911
X4A	Multiwavelength anomalous diffraction analysis of crystalline biological macromolecules	4-30	Howard Hughes Med In	C Ogata 7435 516-282-4938	W Hendrickson 4938 212-305-3456

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X4B	(Conceptual)				
X4C	Diffraction measurements from biological macromolecules	8-15	Howard Hughes Med In	C Ogata 7435 516-282-4938	W Hendrickson 4938 212-305-3456
X5A	Laser Electron Gamma Source (LEGS); medium energy nuclear physics	80-400 MeV	BNL-Physics	A Sandorfi 516-282-7951	A Sandorfi 516-282-7951
X5B	Diagnostic				
X6A	Time and space resolved dispersive x-ray spectroscopy	6.5-20	ANL Brooklyn Coll - CUNY	P Lee 3955 516-282-5934	P Montano 708-252-6239
X6B	X-ray scattering	2.4-21.0	ANL Temple U Northwestern U Brooklyn Coll - CUNY BP Amer Eastman Kodak	K Huang 5498 516-282-5498	P Montano 708-252-6239
X7A	Structural char. through powder diffraction	5-45, WB	BNL-NSLS BNL-Physics Amoco Corp Carnegie Inst of Was E I DuPont Mobil UOP	D Cox 3808 516-282-3818 Q Zhu 5065 516-282-3818	D Cox 3808 516-282-3818
X7B	Crystallography; wide angle scattering	5-21	BNL-Chemistry Swedish Nat Res Coun U of Pittsburgh U of Helsinki	J Hanson 4378 516-282-4381	T Koetzle 516-282-4384
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	M Sagurton 516-282-5708	R Blake 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 5025 516-282-5608	G Idzorek 7245 505-667-8848 E Westbrook 708-252-3983
X9A	XAS	3.4-18.6	U City Sci Center	M Sullivan 516-282-3800 Y Hai 3800 215-386-1912	R Fischetti 3800 215-386-1912

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X9B	Scattering; XAS; diffraction	2.1-18.8	U City Sci Center	R Fischetti 3800 215-386-1912	Y Hal 3800 215-386-1912 M Sullivan 3800
X10A	Diffraction; small angle scattering; crystallography; scattering	2-15.2	Exxon	K Mohanty 5644 516-282-5644	K Liang 908-730-3032
X10B	Scattering; crystallography	8, 12	Exxon	B Zhang 3553 516-282-3553	K Liang 908-730-3032
X10C	EXAFS	3.5-24.7	Exxon	M Sansone 5759 201-730-3388	G Meitzner 4828 908-730-2795
X11A	EXAFS	4.5-35	No Carolina St U U of Connecticut BNL-NSLS Naval Res Lab Mobil E I DuPont Hoechst Celanese	G Lamble 7734 516-282-7734	D Sayers 7731 919-515-4453
X11B	EXAFS	1.7-8	No Carolina St U U of Connecticut BNL-NSLS Mobil E I DuPont Naval Res Lab Hoechst Celanese	G Lamble 7734 516-282-7734	D Sayers 7731 919-515-4453
X12A	Instrument development		BNL-NSLS	P Siddons 5627 516-282-2738	P Siddons 5627 516-282-2738
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 2792 516-282-2792	M Capel 2792 516-282-2792
X12C	Protein crystallography	7-13	BNL-Biology	R Sweet 3401 516-282-3401	R Sweet 3401 516-282-3401
X13	R&D optics development; soft x-ray utilization		BNL-NSLS	E Johnson 4603 516-282-4603	E Johnson 4603 516-282-4603

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X14A	Scattering; crystallography; spectroscopy	3.5-40	Oak Ridge Natl Lab Dow Chem U of Illinois	P Zschack 2583 516-282-5614	P Zschack 2583 516-282-5614
X14B	(Conceptual) X-ray microprobe; x-ray micro-focussing; micro-diffraction	WB	Oak Ridge Natl Lab Dow Chem IBM ATT		
X15A	X-ray standing waves	3-20, WB	ANL Northwestern U Harvard U	P Lyman 7395	M Bedzyk 708-252-7763
X15B	SEXAFS EXAFS	1.5-15	ATT	S Schuppler 2686 516-282-3565	P Citrin 908-582-5275
X16A	Surface diffraction	4-12	ATT U of Illinois	P Eng 5793 516-282-5793	K Evans-Lutterodt 908-582-2154
X16B	Diffraction	7.85	ATT	A MacDowell 5334 516-282-5334	E Isaacs 908-582-7261
X16C	Novel spectroscopy; diffraction	3-16	ATT U of Illinois	D Adler 2686 516-282-2686	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 SUNY@SB U of Chicago BNL-DAS BNL-Medical	N Lazarz 3519 516-282-3519 J Hastings 3930 516-282-3930	J Hastings 3930 516-282-3930
X17B2	Medical research: Angiography; computed tomography; radiotherapy	33.02,33.3	BNL-NSLS SSRL Stanford U No Shore U Hosp LBL BNL-Medical U of Tennessee SUNY@SB	N Gmur 2490 516-282-2490	W Thomlinson 3937 516-282-3937

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X17C	Hi P research; energy dispersive diffraction from microscopic sample volumes	10-100, WB	Naval Res Lab Carnegie Inst of Was Los Alamos Natl Lab ATT SUNY@SB U of Hawaii LLNL	J Hu 7683 202-686-2410	E Skelton 202-767-3014 H Mao 202-686-2467
X18A	Diffuse and surface scattering	4-20	Purdue U Northwestern U U of Illinois U of Missouri	S Ehrlich 7862 516-282-7862	G Liedl 317-494-4100
X18B	EXAFS; optics char.; reflectivity measurements	4-26	ANL AlliedSignal UOP Chevron	S Khalid 7597 516-282-7597	P Montano 708-252-6239
X19A	XAS; EXAFS	2.1-23.0	BNL-NSLS UCA@Davis U of Kentucky U of Michigan BNL-DAS	F Lu 2338 516-282-2338	L Furenlid 5699 516-282-5699
X19C	Topography; liquid surface scattering	4-25, WB	BNL-NSLS SUNY@SB Johns Hopkins U U of Illinois Army Research Lab U of Pennsylvania Adelphi U	M Dudley 516-632-8500	M Dudley 516-632-8500
X20A	Scattering (hi Q-res)	6.3-12	IBM MIT	J Jordan-Sweet 5313 914-945-3322	B Stephenson 914-945-3008
X20B	Scattering at fixed energy	17.36	IBM MIT	J Jordan-Sweet 5313 914-945-3322	B Stephenson 914-945-3008
X20C	Scattering (hi and low Q res)	4-11	IBM MIT	J Jordan-Sweet 5313 914-945-3322	B Stephenson 914-945-3008
X21	High energy resolution inelastic scattering	9-17.5	BNL-NSLS ESRF ATT BNL-Physics Exxon	C Kao 4494 516-282-4494	C Kao 4494 516-282-4494

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X22A	In-plane diffr. & refl. studies of surfaces under electro-chem. cond., and thin films and multilayer	10 Nom.	BNL-Physics BNL-DAS	D Gibbs 4608 516-282-4608	D Gibbs 4608 516-282-4608
X22B	High resolution x-ray diffraction	5-10	BNL-Physics Harvard U	B Ocko 4299 516-282-4299	D Gibbs 4608 516-282-4608
X22C	Diffraction studies of magnetic and structural phase transformations; surface scattering	3-12	BNL-Physics	D Gibbs 4608 516-282-4608	D Gibbs 4608 516-282-4608
X23A2	EXAFS	5.4-30	NIST	J Wolcik 5236 516-282-5823	J Wolcik 5236 516-282-5823
X23A3	Monochromatic topography, small-angle scattering	5-30	NIST	D Fischer 5177 516-282-5177	G Long 301-975-5975
X23B	EXAFS; scattering; crystallography	3-11	Naval Res Lab	J Kirkland 2258 516-282-2258	T Elam 202-767-3014
X24A	Atomic, molecular, and optical physics with x-rays	1.8-5.0	NIST ANL	B Karlin 7863 516-282-5624 S Southworth 301-975-4850	R Deslattes 301-975-4841 P Cowan 708-252-4055
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	4-30, WB	BNL-NSLS ANL ATT BNL-Biology BNL-Physics IBM Harvard U	L Berman 5333 516-282-5333	L Berman 5333 516-282-5333
X26A	Dev. and application of analytical techniques (e.g. microprobe)	4-20	BNL-DAS U of Chicago	K Jones 4588 516-282-4588	K Jones 4588 516-282-4588

Beam line	Research Program	Energy (keV)	Affiliation	Local Contact	Spokesperson
X26C	Dev. and applc. of x-ray microscopy techniques; Laue diffraction protein crystallography	4-15, WB	BNL-DAS U of Chicago ANL	K Jones 4588 516-282-4588	K Jones 4588 516-282-4588
X27A	Instrument development		BNL-NSLS	P Siddons 5627 516-282-2738	P Siddons 5627 516-282-2738
X27B	Instrument development		BNL-NSLS	E Johnson 4603 516-282-4603	E Johnson 4603 516-282-4603
X27C	Instrument development		BNL-NSLS	P Siddons 5627 516-282-2738	P Siddons 5627 516-282-2738
X28A	Instrument development; vacuum research		BNL-NSLS	P Stefan 5728 516-282-2117	P Stefan 5728 516-282-2117
X28B	Diagnostic		BNL-NSLS	P Stefan 5728 516-282-2117	P Stefan 5728 516-282-2117
X28C	Instrument development		BNL-NSLS	P Stefan 5728 516-282-2117	P Stefan 5728 516-282-2117
X29A	(Unassigned)				
X29B	(Unassigned)				
X30	Diagnostic				

VUV BEAMLINES

Beamline U1

An Electron-Yield and Fluorescence-Yield NEXAFS Investigation of Compositions and

Reactivities of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ Powder Catalysts

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An Electron-Yield and Fluorescence-Yield NEXAFS Investigation of Compositions and Reactivities of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ Powder Catalysts

J.G. Chen, B.D. DeVries, J.T. Lewandowski and R.B. Hall

As demonstrated by several research groups, lithium nickel oxides, $\text{Li}_x\text{Ni}_{1-x}\text{O}$, are among the most selective type of catalysts for the conversion of methane to C2 hydrocarbons. In an effort to understand the nature of the active sites for the oxidative coupling of methane, we have applied Near-Edge X-Ray Absorption Fine Structure (NEXAFS) to characterize the surface and bulk properties of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ catalysts. In our experimental set-up, NEXAFS spectra of powder materials could be obtained by measuring the intensity of either electron-yield or fluorescence-yield. While the electron-yield method is sensitive only to the top few atomic layers, the fluorescence-yield method can detect species up to a few thousands angstroms deep into the bulk structure. Such a direct comparison allowed us to observe some significant differences in the surface and bulk compositions of various $\text{Li}_x\text{Ni}_{1-x}\text{O}$ samples, and therefore enabled us to obtain some fundamental understanding concerning the oxidative coupling of methane with lithium nickel oxides catalysts.

For example, a comparison of oxygen K-edge NEXAFS spectra by means of electron-yield and fluorescence-yield is given in Figure 1 for a $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$ sample. It is clear from the comparison that the surface composition (electron-yield measurement) is significantly different from that of the bulk (fluorescence-yield measurement). The characteristic oxygen K-edge features of several compounds, NiO , Li_2CO_3 and $\text{Li}_x\text{Ni}_{1-x}\text{O}$, are shown in Figure 2. By comparing Fig. 1 with Fig. 2, one can readily conclude that, although the bulk composition of this sample is $\text{Li}_x\text{Ni}_{1-x}\text{O}$, the surface composition is in the form of Li_2CO_3 .

Figure 1

Figure 2

Fluorescence Yield NEXAFS of a Buried Metal / Polymer Interface: DVS bis-BCB (divinyl siloxane bis-benzocyclobutene)

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DVS bis-BCB (divinyl siloxane bis-benzocyclobutene) is used for dielectric layers in new generation multilayer interconnect devices (multi-chip modules) [1]. For this application it is important to understand the nature of the bonding and complexing which occurs at the metal / polymer interface. The depth sensitivity (about 200 nm) and the non-destructive nature of fluorescence yield are particularly useful in studying the buried interface between DVS bis-BCB coated with aluminium (10 to 100 nm)[2]. In contrast the relatively short depth sensitivity of traditional electron yield USXAS makes it useless for the buried interface study, since it would only probe the outer 5nm of the aluminium overlayer. We have collected FY carbon K near edge spectra for evaporated aluminium coated (50 nm thick) DVS bis-BCB (50 nm thick) as well as the identical bare polymer. The figure, left and right panels show these normalized spectra for normal and glancing incident x-rays respectively. In order to enhance the metal / polymer interface sensitivity each panel shows a difference plot (coated polymer minus bare polymer). The C-C π^* peak (286 eV) of the aromatic ring of DVS bis-BCB in the difference plots appears to undergo a dramatic enhancement in polarization dependence after the formation of the metal / polymer interface. This polarization enhancement at the interface region implies that the aromatic ring planes of DVS bis-BCB are highly oriented towards the surface normal. These preliminary results highlight the use of ultra soft x-ray absorption spectroscopy to provide new detailed chemical information which may be useful in predicting and optimizing the adhesion in metal / polymer interfaces.

1. T.M. Stokich, Jr., W.M. Lee and R.A. Peters, Materials Research Society Proceedings 227, 103(1991).
2. Manuscript in preperation for submission to Science.

U1

Steric Acid Absorbed on Polycrystalline Copper: An Initial NEXAFS Study of Tribochemical Effects

D. A. Fischer (NIST), Z. S. Hu (NIST), and S. M. Hsu (NIST)

Two monolayer samples of Steric acid on polycrystalline copper were produced using the Langmuir-Blodgett technique. One of these samples was then rubbed on a well polished copper plate in order to induce tribochemical effects on the sample surface. Polarization dependant NEXAFS above the carbon K edge was performed on both of these samples using partial electron yield in order to study any surface induced orientational or chemical changes. Chemical changes have been observed in this system using infrared microspectroscopy and surface enhanced raman spectroscopy.

The electron yield data for the unrubbed sample is shown below and strongly suggests that the carbon chain (CH₂) axis is oriented towards the surface normal, and that is nearly standing up straight from the surface. This is supported by near edge features characteristic of the sigma* C-H and C-C bonds. This orientation was observed for both of the samples supplied, rubbed and unrubbed. The C=O pi* peak has a weak polarization dependance indicating a tilt angle of about 35 degrees from the surface normal. Finally it appears that the near edge peaks from the C-C and C-H bonds of the chain get reduced after the film is rubbed.

The authors would like to gratefully acknowledge the Exxon PRT for contributing U1 PRT beamtime for this experiment.

U1

Soft X-Ray Fluorescence Oxygen K Edge NEXAFS of Oxygen-Reduced High-Tc Superconductors

A. R. Moodenbaugh (BNL) and D. A. Fischer (NIST)

We studied the oxygen K near edge of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. Previously we determined the x variation of the oxygen K pre-edge features in polycrystalline $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (2:1:4) system to elucidate the hole state density using bulk-sensitive fluorescence yield NEXAFS. In the 2:1:4 system oxygen hole density is varied both by Sr doping (previously reported by us) or by adjustment of oxygen content. In the figure below, the dependence of the oxygen K near-edge features are shown for standard and oxygen-reduced 2:1:4 samples with having Sr contents $x=0.35$ and $x=0.50$. The figure also shows for comparison the pre-edge feature of the unreduced Sr $x=0.60$ and $x=0.00$.

The qualitative observation is that the pre-edge features of the reduced $x=0.35$ and $x=0.50$ samples have two pre-edge features which are characteristic of optimally doped ($x=0.15$), high- T_c samples. However, the qualitative similarity of the pre-edges of the reduced $x=0.35$ and $x=0.50$ samples compared with the fully oxidized optimum doped samples ($x=0.15$) does not correlate with superconducting properties: the reduced samples are not superconducting.

The energies at which both peaks appear in the NEXAFS of the reduced samples are shifted higher by approximately 0.5 eV compared with fully oxidized superconducting samples. This suggests that the Fermi Level in the reduced samples is raised relative to that of the unreduced samples. Additional experiments on single crystal samples might shed additional light on this complex issue.

The authors gratefully acknowledge the EXXON PRT for providing U1 PRT time for this experiment.

NEXAFS Study of $C_6H_5I/Cu(111)$

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Determining the adsorption geometry of chemisorbed species is critical to understanding the possible interactions of a molecule with a surface. We have performed C-K edge near edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements on $C_6H_5I/Cu(111)$ and its reactive intermediate $C_6H_5/Cu(111)$ -I. Figure 1 shows the NEXAFS spectra of these species at sub-monolayer coverage. The C_6H_5I sample was produced and recorded at 100 K, while $C_6H_5/Cu(111)$ -I was formed by annealing to 250 K. The spectra were recorded in partial electron yield detection with a retarding voltage of -190 eV. The dotted curves were recorded with the X-ray at glancing incidence; the solid lines are for normally incident light. The polarization dependences of the π^* and σ^* resonances indicate that the plane of the molecule is not perfectly parallel to the surface. The spectra of $C_6H_5/Cu(111)$ -I, upper set of curves in Fig. 1, indicate that the plane of the reactive intermediate is more parallel to the surface than the parent, but still is not perfectly aligned. These results are in contrast to our work on $C_6H_6/Cu(111)$ which showed that the plane of the benzene molecule is parallel to the surface at similar coverage. Figure 2 shows an expanded region of the NEXAFS spectra recorded after annealing to the indicated temperatures. From this data, it is concluded that C-I bond cleavage begins at ≈ 150 K.

Performance Characterization of the U2B Infrared Beamline

G.L. Carr (Grumman), M. Hanfland (Carnegie Inst.), K.M. Thorpe and G.P. Williams (BNL).

U2B began operation in late 1992 as the second IR beamline at the NSLS. Much of the scientific program requires high brightness. Therefore, we have tested the beamline optical performance by measuring the transmitted signal for various apertures down to 50 μm . Fig. (a) shows the beam profile at the spectrometer's $f/3.5$ sample location, indicating a FWHM of about 100 μm . This value is near the limit set by mirror aberrations and the synchrotron's intrinsic source dimensions. We also compared the small aperture infrared signal of U2B with the standard mid-infrared spectroscopy source, a globar. Fig. (b) shows the synchrotron / globar transmitted signal ratio for various apertures across the infrared and demonstrates that U2B provides 10 to 100 times more signal for apertures of 300 μm or less. The remaining figures show ratios of two identical, 50 μm aperture, transmission measurements for each source, and indicate the signal-to-noise. The synchrotron [Fig. (c)] shows a much cleaner line at 100% than the globar [Fig. (d)], demonstrating that U2B provides 10 to 100 times better small aperture performance. The source is clearly well-suited for microspectroscopy.

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U2B

SYNCHROTRON INFRARED ABSORPTION MEASUREMENTS OF HYDROGEN AT MEGABAR PRESSURES

M. Hanfland, R.J. Hemley, and H.K. Mao (Geophysical Lab. and CHiPR, CIW)

Absorption spectra of solid molecular hydrogen have been studied at high pressures and low temperatures using Fourier transform techniques and synchrotron radiation from the newly built infrared (ir) beamline U2B. Absorption spectra at 85 K and pressures upto 216 GPa are presented in Figure 1. The broad band at $\sim 4500 \text{ cm}^{-1}$ can be assigned to the $Q_1(J)$ ir vibron. The pressure dependence of the frequency of the ir vibron is compared to that of the $Q_1(J)$ Raman active vibron in Figure 2. The discontinuous shift of the Raman vibron to lower frequencies at 150 GPa has been discovered previously. The discontinuity disappears above 140 K and has been attributed to a phase transition. The infrared absorption measurements reveal a similar discontinuity for the ir vibron. The magnitude of the discontinuity is the same in both ir and Raman measurements. Further the vibron absorption increases by several orders of magnitude at the discontinuity (Fig. 1). These results indicate a significant change in the electronic properties of hydrogen at the 150 GPa transition, while the intermolecular vibrational coupling remains unchanged. An additional line appearing at 110 GPa 45 cm^{-1} below the vibron band provides evidence for a previously not observed phase transition.

Figure 1. Absorption spectra of hydrogen at 85 K in the frequency range of the $Q_1(J)$ ir vibron. (a) low pressure phases, (b) high pressure phase

Figure 2. Ir and Raman vibron frequencies as a function of pressure at 85 K. Open circles, pressures estimated on basis of extrapolation of lower pressure data; small squares, new line appearing at 110 GPa; dashed lines, 295 K.

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U2B

IR TRANSMISSION OF THICK C_{60} SINGLE CRYSTALS: HIGHER ORDER MODES

Michael C. Martin, Xiaogun Du, Daniel Koller, and Laszlo Mihaly (SUNY @ Stony Brook)

We report the measurement of the mid-infrared transmission of large C_{60} single crystals. Spectra of thin film C_{60} show the four F_{1u} vibrational modes allowed by symmetry¹. But when our crystals are thick enough, the spectra exhibit a very rich structure with over 120 vibrational absorptions visible in the $100 - 4000 \text{ cm}^{-1}$ range. The figure below shows a typical spectra, including the far-IR portion ($100 - 600 \text{ cm}^{-1}$) obtained at beamline U4IR. Many silent modes are observed to have become weakly IR active, probably due to isotopic impurities breaking the I_h symmetry of the pure C_{60} molecule. In addition we observe a large number of higher order combination modes.

The new U2B beamline allowed us to measure our C_{60} crystals with much better resolution (0.3 cm^{-1}) and with less integration time due to the brightness of the Light Source than our conventional spectrometer. We used a liquid helium flow cryostat to measure the infrared spectra as a function of temperature. We were also able to use the tight focus of the IR beam to measure through an optical diamond anvil cell, thus measuring the infrared vibrations as a function of pressure up to 25Kbar [Ref 2].

The combination of both temperature and pressure dependence of the large number of weak modes greatly aided our effort to determine the modes' symmetry assignments. By carefully analyzing the higher order vibrations and using group theory considerations, we assigned candidate frequencies for the F_{1g} vibrations and to the F_{2u} , G_u , H_u group of odd-parity vibrations³.

This work is supported by NSF Grant DMR 9202528.

1. Michael C. Martin, Daniel Koller, and L. Mihaly, Phys. Rev. B 47, 14607 (1992); W. Kratschmer *et al.*, Nature 347, 354 (1990).
2. Michael C. Martin, John Kwon, Xiaogun Du, and L. Mihaly, to be published.
3. Michael C. Martin, Xiaogun Du, and L. Mihaly to be published.

Surface Sensitivity of PES for Cerium Heavy Fermion Compounds

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In a previous study, we reported our failure to observe the Kondo Resonance (KR) in Ce and Yb based heavy fermion compounds [1]. The inclusion of crystal field effects and finite U do not improve the agreement with theory significantly. Other possible explanations for these null results have focused on the surface contribution in PES. The escape depth in rare earth compounds is believed to be on the order of 3-4 atomic layers and it is not known to what extent the near surface region exhibits heavy fermion behavior. In order to better characterize the surface, we have undertaken careful dosage studies in the submonolayer regime $<1\text{L O}_2$. For Ce compounds we find that the lineshape, spectral weight and binding energy of the 4f features is extremely sensitive to small amounts of contamination. For CeCu_2Si_2 ($T_K = 8\text{K}$) and CeSn_3 ($T_K = 150\text{K}$) the tail of the KR and its spin-orbit sideband ($f_{5/2}$ and $f_{7/2}$) are quenched by $\sim 0.5\text{L O}_2$ while the 2 eV feature (f_0) grows and shifts toward the Fermi level as the dioxide layer forms (Fig. 1). This makes analysis of Ce heavy fermions more problematic than Yb compounds because in the latter the surface and bulk are easily distinguished ($\Delta_{\text{sb}} \sim 5\text{ eV}$) and the surface components are readily quenched by dosing. Despite apparently substantial contamination, perfect agreement with the KM has been claimed by other groups for CeCu_2Si_2 (Fig. 2 - inset from Ref. [2]).

Figure 1

[1] J.J. Joyce, et. al., PRL 68, 236 (1992); [2] J.W. Allen, et. al., Adv. Phys. 35, 275 (1986)

Figure 2

Hole Occupancy in Ytterbium Heavy Fermion Compounds

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The Gunnarsson-Schonhammer (GS) solution to the Anderson Impurity Hamiltonian (AIH) derives relations between two key observables which can be determined by PES: 1) n_f the hole occupancy in Yb compounds determined by the ratio of trivalent to divalent intensities and 2) T_K the Kondo temperature given by the binding energy and width of the $4f_{7/2}$ peak. Since acceptable values of n_f fall in the range $.7 < n_f < 1$, the spin fluctuation limit of the AIH, the PES measurement serves as a check on the applicability of the AIH to Heavy Fermion (HF) compounds. Our data yields n_f values which are closer to the mixed-valent regime and exhibit a trend opposite to the expected inverse relation between n_f and T_K : YbAl_3 $n_f \sim .6$ ($T_K = 400\text{K}$), YbCu_2Si_2 $n_f \sim .55$ ($T_K = 40\text{K}$) (Fig. 1). This n_f for YbAl_3 is in accord with [1] but disagrees with [2] and with XAS measured at the L_{III} edge [3]. More striking inconsistencies are revealed when we compare the spectral weights between Yb compounds YbAgCu_4 ($T_K = 100\text{K}$) and YbAuCu_4 ($T_K = 5\text{K}$). GS calculations at $T=0$ indicate that the intensity of the divalent 4f features (Fig. 2) should be in a ratio of $\sim 1:40$ whereas the data show the ratio to be $\sim 1:2$. This disagreement becomes even more glaring when one factors in the measuring temperature of 80K which is $160T_K$ for the latter compound, i.e., the Kondo resonance should be renormalized to zero, implying a error in the calculated result of $> 10^2$, strongly at odds with the theory.

Figure 1

[1] E-J Cho, et. al., Physica B 186-8, 70 (1993); [2] H. Tjeng, PRL 71, 1419 (1993); [3] J. Lawrence, et. al., to appear in Physica B (1994)

Figure 2

U3C

Temperature Dependence of 4f States in Ytterbium Heavy Fermion Compounds

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The Non-Crossing Approximation (NCA) treatment of the Anderson Impurity Hamiltonian (AIH) makes specific predictions about the temperature dependence of the 4f States or Kondo Resonance (KR), in Ytterbium heavy fermion compounds. We have studied two materials which span a wide range of Kondo temperatures (T_K), for which the following increases in spectral weight of the KR between $T=300\text{K}$ and $T=80\text{K}$ are calculated within the NCA model: 1) YbAl_3 ($T_K=400\text{K}$) 95% 2) YbCu_2Si_2 ($T_K=40\text{K}$) 41%. Our data show changes in the integrated intensities which are $\sim 10\%$ for both compounds (Fig. 1), an order of magnitude less than expected, and showing no variation with T_K . No additional temperature dependence is seen between $T=80$ and $T=20\text{K}$ [1]. Since T_K sets the low energy scale, providing a link between high energy spectroscopies and thermodynamic measurements, this finding is a serious discrepancy. We also note that the width and binding energy of the KR is independent of T_K , whereas it should scale as $k_B T_K$. Lineshape analysis of the bulk levels reveals striking similarities with the 4f levels in pure Yb and with core-like Lu 4f states in LuAl_3 , with only the surface components showing substantive differences. Furthermore the temperature dependence of the bulk 4f levels in Yb films is similar to that of the single crystals (Fig. 2). These observations point to invariant 4f electron character and suggests an alternate explanation in terms of more familiar mechanisms such as phonon broadening and thermal expansion.

Figure 1
[1] R.I.R. Blyth, et. al., to appear in Phys. Rev B Oct. 1993

Figure 2

U3C

EVIDENCE FOR THE EXISTENCE OF BULK Sm^{2+} IN SmSn_3

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Most of the rare earth compounds showing the Kondo effect are alloys of either Ce or Yb. An exception is the samarium alloy SmSn_3 . It has been suggested that the Sm in this material is entirely trivalent but the evidence from core level XPS is inconclusive, largely because the surfaces of most, if not all, Sm compounds contain divalent Sm. We have used angle-resolved resonant photoemission to attempt to solve this question. By varying the detected electron emission angle we can tune the surface sensitivity of our measurements, with normal emission being the most bulk sensitive, and grazing emission the most surface sensitive. The figure shows that at all angles we see signal from both divalent and trivalent Sm, and that the ratio of divalent to trivalent does not increase at grazing emission. Thus it appears that the divalent Sm ions are not concentrated at the surface and hence bulk SmSn_3 contains some divalent Sm.

In addition, we have measured X-ray absorption spectra (XAS) at the samarium 4d edge. Unlike the photoemission results these measurements are not surface sensitive. We find that photon energies which give maximum photoemission intensity in the divalent Sm peaks correspond to features in the 4d XAS spectra. This provides further evidence that the bulk material does in fact contain finite amounts of divalent Sm. We are unable to determine the $2+ / 3+$ ratio from the photoemission results since the resonant energies for the two states are different, hence the photoemission cross sections are not the same.

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ELECTRONIC STRUCTURE AND AUGER LINESHAPES OF $\text{Au}_x\text{Pd}_{1-x}$

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We have studied the electronic structure of the disordered alloy system $\text{Au}_x\text{Pd}_{1-x}$. We used the Cooper minima of the Au 5d and Pd 4d bands to identify their contributions to the DOS. We find (fig. 1) that recent KKR-CPA calculations give excellent agreement with our results, but that earlier calculations show serious discrepancies. In addition we measured the Au N6,7VV and Pd M4,5VV Auger lineshapes. We find that one-electron lineshape calculations using the KKR-CPA give reasonable agreement with the Au spectra. For the Pd spectra (fig. 2) the calculations give poor agreement at low Pd concentrations. We suggest that this is due to the neglect of many body interactions, which are likely to be increase in strength as the Pd d-band narrows, rather than any intrinsic problem with the KKR-CPA. A full Cini-Sawatzky calculation may well give better results, as this method has successfully modelled the Pd Auger spectra from AgPd.

Work supported by U.S. D.O.E.

Fig. 1

Fig. 2

THE RECONSTRUCTION OF Ni(111) INDUCED BY THE ADSORPTION OF ATOMIC SULFUR

D. R. Mullins (Oak Ridge National Lab)

In general, on most single crystal metal surfaces, atomic sulfur adsorbs in the highest coordination site available at low coverage. As the coverage increases adsorbate-adsorbate interactions or surface strain causes the adatoms to adopt lower coordination sites or results in surface reconstruction. Low energy alkali ion scattering has demonstrated that atomic sulfur adsorbs in the fcc hollow site on Ni(111) at coverages up to 0.25 ML [1]. At coverages between 0.25 and 0.40 ML the six-fold symmetry of the surface is lost indicating reconstruction of the top layer of Ni atoms.

S 2p core level photoemission has been used to help elucidate the structure of the reconstructed surface. At coverages up to 0.25 ML a single, well resolved S 2p state is observed with a S 2p_{3/2} binding energy of 161.15 eV (Fig. 1). This is assigned to sulfur adsorbed in a three-fold hollow site on an unreconstructed surface. At 0.25 ML the S 2p signal becomes very broad and consists of at least three states. At coverages above 0.3 ML the S 2p signal becomes sharper and can be fit to two states with S 2p_{3/2} binding energies of 161.60 eV and 162.25 eV. On other metal surfaces, a relationship has been observed between the S 2p binding energy of atomic S and the coordination of the S to the surface. The higher the coordination, the higher the S 2p binding energy. The shift of the S 2p signals to higher binding energies observed at high coverages on Ni(111) indicates that the surface has reconstructed resulting in higher coordination bonding sites. A proposed model for the surface at 0.40 ML is shown in Fig. 2. The surface is predominately reconstructed into a four-fold structure with periodic troughs occurring between the four-fold plateaus. The 161.60 eV signal is associated with S on top of the plateaus and the 162.25 eV signal comes from S in the troughs where the adatoms can bond to the second layer Ni atoms.

Fig. 2

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ADSORPTION AND REACTION OF CH₃SH ON SULFUR AND CARBON COVERED W(001)

D. R. Mullins and P. F. Lyman (Oak Ridge National Lab)

The adsorption and reaction of methanethiol, CH₃SH, has been studied previously on the clean W(001) surface by S 2p soft x-ray photoelectron spectroscopy. It was observed that methyl thiolate, CH₃S, was rapidly formed at 100 K at all thiol coverages up to the formation of a second layer. Two distinct thiolate species were identified in the S 2p spectra and were assigned to thiolates adsorbed in high- and low-coordination sites on the surface. The reactivity of the two sites was very different with the species in the low-coordination site being less reactive as indicated by the temperature at which the thiolate S 2p signal converted into an atomic sulfur S 2p signal. It was hypothesized that less electron transfer from the substrate into the thiolate antibonding orbital occurred in the low-coordination site thus increasing its stability. Modifying the surface with atomic adsorbates allows us to selectively block certain adsorption sites and to alter the surface electronic properties.

Preadsorption of atomic S blocks the adsorption of CH₃SH and thus the formation of CH₃S. At low atomic S coverages the site blocking is selective. At 0.25 ML of preadsorbed S, virtually all of the thiolate is bonded in low-coordination sites as observed in the S 2p spectra. The chemistry of CH₃SH was not dramatically altered, however. The branching between non-selective total decomposition and selective decomposition to form methane remains the same as the S coverage is increased. The stability of the C-S bond is also not dramatically altered. This indicates that although atomic S can block adsorption sites, it does not alter the reaction selectivity through a stabilization of the C-S bond.

Preadsorption of atomic C does not reduce the overall reactivity of the surface toward the adsorption of CH₃SH. As with the preadsorption of S, atomic carbon forces the thiolate to bond in low coordination sites. The selectivity of the CH₃SH decomposition is dramatically different with methane production increasing by 75% while total decomposition decreases by 50%. In addition, rehydrogenation of the thiolate to form methanethiol is observed above 300 K. Changes in the surface chemistry are evident in the S 2p and C 1s spectra. A small amount of chemisorbed CH₃SH is formed at 100 K which decomposes into CH₃S as the sample is heated to 300 K. The C-S bond is more stable than on the clean surface. There is also evidence of surface methyl formation which is hydrogenated at high temperatures to form methane. The conclusion is that preadsorbed C does not block adsorption on the surface but it does reduce the ability to cleave all of the bonds in the methanethiol molecule. Reaction sites are also available which enhance the selective chemistry over the total decomposition of the molecule.

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Surface Chemistry of PH₃, PF₃ and PCl₃ on Ru(0001)

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Soft X-ray Photoelectron Spectroscopy has been used to study the adsorption, desorption and decomposition mechanisms of PH₃, PF₃ and PCl₃ on Ru(0001). Large chemical shifts in the P2p binding energy for individual PX_n species, X = H, F, Cl and 0 ≤ n ≤ 3 allow the quantitative identification of surface intermediates as a function of surface temperature and initial reactant exposure. Representative data are illustrated in the figure for adsorption of the three gases at 150K. In Fig. 1a, the single spin-orbit split peak at 133.4 eV binding energy (P2p_{3/2}) is indicative of molecular PF₃ adsorption. Electron and photon irradiation induces sequential defluorination [1], as indicated by fig. 1b. Discrete peaks are observed for each of the PF₂, PF and P surface species, with approximately equal increments of binding energy shift per F atom removed.

In contrast, both PH₃ and PCl₃ adsorb dissociatively at 150K, as shown by figs. 1c and 1d, respectively. Both atomic phosphorus and an unspecified PH_x moiety co-exist with the parent PH₃ molecule. For PCl₃, the major dissociation intermediate is PCl. Evidence for two, chemically inequivalent PCl₃ species is found by lineshape fitting of the dominant peak near ~133 eV. These are postulated to originate from molecules bonded directly to Ru(0001) and others in condensed layers. These results show that PF₃ is more stable than either PH₃ or PCl₃ on Ru(0001) at 150K. Using this and other temperature-dependent data, a thermochemical analysis allows important energetic parameters to be extracted [2], thereby yielding insights into the chemistry of these isostructural molecules.

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ALKALI METAL ADSORPTION ON TRANSITION METAL SUBSTRATES: Na and Rb on Ta(110).

A. B. Andrews and G. K. Wertheim (AT&T Bell Laboratories)

As part of a continuing program on the reaction of alkali adsorbates with metals and semiconductors, which began with work on W(110) [1], we have investigated the adsorption of Na and Rb on Ta(110). To obtain a clean Ta surface a single crystal was sputtered and then annealed very close to the melting point by rear-surface electron bombardment [2]. The crystal was then cooled to 78K and exposed for controlled intervals to Na or Rb vapor from well degassed SAES Getters sources. The coverage was calibrated using the initial appearance of a second alkali signal at larger binding energy, which originates from the second alkali layer. The work function cut-off was used to check the coverage calibration. Photoemission data for the Ta $4f_{7/2}$ and Na 2p or Rb 4p levels were taken as a function of coverage. Data obtained for the Ta $4f_{7/2}$ level at saturation coverages are compared with those of the clean surface in Fig. 1. Note that there are no significant changes in line shape with alkali coverage. The most startling result is that the surface-atom core-level shift is actually *increased* by the adsorbed alkali.

The data were analyzed by fitting each line with a Doniach-Sunjić function convolved with a Gaussian. The change in average surface-atom core-level shift induced by alkali coverage is shown in Fig. 2, together with the results of earlier work for W(110). The fact that the alkali-induced shifts are positive, i.e., opposite to what is naively expected for charge transfer from the alkali adsorbate to the conduction band of the substrate, indicates that this is not the correct adsorption mechanism. Such positive shifts are more readily understood in the light of a more recent theory of the alkali-metal interaction developed by Ishida and Terakura [3]. Their calculation show that the s-electron charge of an adsorbed alkali resides in a charge cloud located between the surface of the metal and the alkali core. The photoemission data from the shallow p core levels of the alkali adsorbate indicate that this charge cloud is dominated by alkali s-character.

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Electronic Structure of Defects in a Quasi-One Dimensional Oxide Conductor.

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and Martha Greenblatt and William McCarroll, Department of Chemistry, Rutgers University.

Our General User program is aimed at understanding the electronic and structural properties of quasi-low dimensional oxide conductors. These are ternary transition metal oxides that exhibit essentially one dimensional (1D) physical characteristics, including Peierls transitions. Due to the large size of the crystals, these oxides allow unique spectroscopic measurements to be made of 1D solid systems. We have undertaken both ARP and core level measurements of the electronic structure of these oxides. The structure of Fermi surfaces is of particular interest since they play a dominant role in determining many of the properties of these materials. As part of this program, the first quasi-1D Fermi surface for an oxide conductor ($\text{Li}_{0.9}\text{Mo}_2\text{O}_7$) was determined.¹ Current efforts are aimed at measuring band structure changes as the oxides are cooled through the Peierls transition. $\text{K}_{0.3}\text{MoO}_3$ is the first oxide studied since the Peierls transition occurs at an easily accessible 180 K. In the course of these experiments, we discovered that $\text{K}_{0.3}\text{MoO}_3$ is extremely sensitive to defects produced by photon stimulated desorption (PSD). Figure 1 shows normal emission spectra taken with 18 eV photons from cleaved $\text{K}_{0.3}\text{MoO}_3$. Spectrum (a) is that obtained from the cleaved surface. Emission below E_F originates from the Mo 4d states, and it is well separated from emission from the O 2p states which has its onset at approximately 2.3 eV. Spectrum (b) is that from the same spot on the surface after exposure to the 18 eV beam for 20 hours. Clearly the emission in the band gap between the Mo 4d and O 2p features has increased significantly. The origin of this damage is PSD via second order light at 36 eV. (which is above the Mo $4p \rightarrow 4d$ absorption threshold). This damage mechanism was verified by exposing the sample to first order light above threshold at 60 eV. Spectra (c) and (d) show the radical changes in electronic structure that occur due to this exposure. PSD can thus be used to create elementally specific defects. Investigating the role of defects in modifying Fermi surfaces and charge density wave transport in these systems is a major thrust of this program. We now have a method of defect production other than simple ion bombardment. The latter mechanism results in the initial removal of K atoms from the surface, causing the surface to become less metallic, with the subsequent removal of O atoms reducing the surface, and causing it to become more metallic.

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1. K.E. Smith, K. Breuer, M. Greenblatt and W. McCarroll, Phys. Rev. Lett. **70**, 3772 (1993).

Fig. 1. APR spectra from UV irradiated $\text{K}_{0.3}\text{MoO}_3$ taken with $h\nu = 18$ eV. a): cleaved; b): 20 hours @ $h\nu = 18$ eV; c): 60 min. @ $h\nu = 18$ eV; d): 145 min. @ $h\nu = 60$ eV.

COVALENT EFFECTS IN ALKALI ADSORPTION ON Ta(110)

E. Kneeder and S. D. Kevan (*Physics Department, University of Oregon*)

Despite long-standing interest in addition to substantial experimental and theoretical attention, the adsorption of alkalis on nominally clean metal surfaces remains a very controversial topic. At low concentration, the central issue concerns whether the bonding is predominantly "ionic" so that the alkali ionization level is substantially depopulated, or "covalent", wherein bonding is characterized more precisely as charge sharing. We will present the results of a systematic angle-resolved photoemission study of the electronic structure of Li, Na, K, and Cs adsorbed onto Ta(011) which can be largely understood in terms of covalent alkali(ns)-Ta(5d) interactions. A large projected gap centered in the surface Brillouin zone makes the underlying electronic structure simple so that its evolution as a function of alkali coverage can be isolated for study. A nearly dispersionless surface band of $5d_{z^2}$ character exists near the top of this gap just below the Fermi level, E_F . For all alkalis, this shifts smoothly to higher binding energy as a function of alkali coverage. The shift saturates at the work function minimum, and its magnitude decreases monotonically as a function of alkali mass. This implies formation of an occupied Ta(5d)-alkali(ns) bonding level up to 2 eV below E_F whose binding energy increases monotonically with increasing alkali ionization potential. Simultaneously, the effective mass of the surface band decreases, converging in all cases upon a reduced mass near one. This implies substantial alkali-induced lateral delocalization of charge. At higher coverage, a sharp feature appears very close to the Fermi level. Paradigmatic models would ascribe this feature to partial occupation of the alkali ionization level. This, however, no longer exists as a separate entity. Rather, the additional feature must result from formation of a Ta(5d)-alkali(np) or alkali $(n+1)s$ bonding level. Our results are not inconsistent with a significantly polar bond. They do, however, challenge existing notions about resonantly broadened and partially occupied alkali levels.

PROPERTIES OF Cs OVERLAYER ON W(110)

D. M. Riffe and G. K. Wertheim (*AT&T Bell Laboratories*)

The $5p$ spectra of Cs overlayers adsorbed on a W(110) surface were studied by photoelectron spectroscopy in order to elucidate the nature of the alkali-substrate interaction [1]. The question is whether the screening cloud that forms between the metal substrate and the adsorbate is made up of substrate or adsorbate orbitals.

The W surface was prepared by sputtering and annealing and was cooled to 80 K before exposure to Cs vapor from an SAES Getters source. Data up to monolayer saturation, taken with 29.5 eV photons, show a decrease in core-electron binding energy and change from a symmetrical line shape at low coverage to an asymmetrical one as saturation coverage is approached, see Fig. 1. The data were analyzed by fitting them with Gaussian-broadened Doniach-Šunjić lines in order to determine the natural lifetime width of the Cs $5p$ core hole.

The numerical results are summarized in Fig. 2. The decrease in binding energy with increasing coverage is due in part to the dipolar repulsion between the Cs adsorbate atoms and in part to the eventual formation of a two-dimensional Cs $6s$ conduction band. The transition to metallic character at high coverage is clearly seen

in the singularity index. It is small at low coverage, showing that the conduction band of the substrate makes only a small contribution to the asymmetry. It rises to values comparable to those of the surface atoms of alkali metals when the adsorbate conduction band forms.

The most interesting result is the greatly increased Cs $5p_{3/2}$ core-hole lifetime width. It is ten times larger than that in metallic Cs, where it is determined by an $O_3P_1P_1$ Auger process. (Two $6s$ electrons are available for the Auger process by virtue of the conduction-electron screening of the $5p$ hole.) Comparable enhanced decay rates have been observed for all alkali adsorbates on simple, noble and transition metal substrates. They are unlikely to be due to an interatomic Auger process with substrate electrons, but are of the right magnitude for an $O_3P_1P_2$ Auger process within the Cs adsorbate atom. We conclude that the charge that screens the adsorbate atom resides predominantly in adsorbate orbitals at all coverages. It follows that the initial state charge cloud also has alkali s character.

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COMPOUNDS OF Au WITH ALKALI METALS: CsAu and RbAu_x

J. E. Rowe and G. K. Wertheim (AT&T Bell Laboratories)

The lifetime width of outermost p core levels of the alkali metals, which depends on the CVV Auger process, provides a probe of the occupancy of the alkali valence shell. Large widths found in alkali atoms adsorbed on metals have led to the conclusion that there is no charge donation to the substrate. The intermetallic CsCl-structure compound CsAu, in which charge transfer is believed to be close to the ionic limit, provides an opportunity to test this concept.

We have prepared CsAu by exposing a single crystal of Au to Cs vapor from an SAES Getters dispenser, both at 295 and 450 K. The equiatomic compound CsAu is the only intermediate phase in the Au-Cs system, making it favorable for such an experiment. The data taken with 90 eV photons are very similar to those obtained some years ago by XPS [1], see Fig. 1. They are also in very good accord with the results of a band structure calculation [2]. Analysis of the Cs 5p spectrum shows that it consists of two overlapping spin-orbit doublets with lifetime width much smaller than that obtained for Cs adsorbates. They presumably represent bulk and surface Cs.

Unfortunately, the weak component at 9.5 eV limits the accuracy of the lifetime-width determination. This component, which is evident in all previously published work, appears to be intrinsic rather than due to chemical contamination. An explanation of this feature is obtained from data taken after a clean Au sample had been exposed to Rb vapor, see Fig. 1, top. In the Au-Rb system there are three intermediate phases, RbAu₄, RbAu₂, and RbAu. In the presence of a bulk Au substrate it is likely that one of Au-rich compounds will be preferentially formed. The large 5d splitting is then a band-structure effect due to the stronger Au 5d-5d interactions in this compound. The interesting observation is that when the 9.5 eV peak is strong in CsAu, the 5d_{7/2} peak intensity is correspondingly enhanced, i.e., the spectrum look as though there were a component resembling the RbAu_x Au 5d spectrum. It must represent an interfacial Au-rich phase that does not appear in the equilibrium phase diagram. Data taken with 45° take-off angle confirm that it is not a surface effect.

With this assignment of the 9.5 eV peak, a more definitive analysis of the Cs 5p spectrum was carried out. The results indicate that the interatomic Auger decay of the Cs 5p core hole with charge in the largely gold-derived conduction band does not significantly increase the 5p lifetime width.

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INTERFACE FORMATION OF ULTRATHIN C₆₀ FILMS ON Cu(111)

J. E. Rowe, A. B. Andrews and G. K. Wertheim (AT&T Bell Laboratories)

The electronic properties of the interface formed with C₆₀ and Cu(111) have been investigated with high resolution angle-resolved photoemission using synchrotron radiation from the AT&T-NSLS U4A beamline with photon resolution (30 meV) and photoemission resolution (80 meV). Low energy electron diffraction studies performed *in situ* of C₆₀ on Cu(111) show that well-ordered overlayers were grown of thickness ~1-10 monolayers with

single-domain epitaxy. The C₆₀ films were deposited in ultrahigh vacuum ($p \sim 2 \times 10^{-10}$ torr), and we find that for a very thin layer (0-1 monolayers, ML) the Cu substrate plays a role similar to that of K in K₃C₆₀ films confirming previous core-level studies [1]. Typical results for normal emission at photon energy, $h\nu=25$ eV are shown in Figure 1. Curve (a) shows the molecular-like peaks of a thick (~25 ML) film and is similar to data previously reported by several groups. Curve (b) is data for a ~1 ML film of C₆₀ on Cu(111) and curve (c) is data for clean Cu(111). The clean surface shows a weak peak at 0.4 eV below the Fermi level (taken as zero energy) that is stronger at lower and higher photon energy labeled S₁. The features labeled I₁, I₂, and I₃ are assigned to states derived mainly from C₆₀ molecular orbitals shifted somewhat from the peaks of the thick layer. The peak I₁ corresponds to the LUMO derived band first seen for K₃C₆₀ and occurs ~0.15 eV below the Fermi level. Thus Cu atoms donate charge to partially fill the π^* LUMO band. These assignments are further supported by the angular dependent data not shown. The largely Cu derived features at ~2.2, ~2.7 and ~3.8 eV have the expected dispersion even in the presence of the C₆₀ overlayer. The C₆₀ derived features show very weak dispersion in agreement with previous work on bulk single crystals [2]. The peak labeled I₂ shifts by 35 meV in going from normal emission to 12.5° which is near the surface Brillouin zone boundary in the Γ -K direction. In contrast, the I₁ peak shifts by more than 150 meV over the same range. This corresponds to the 2 dimensional bandwidth of this thin interfacial compound and thus is a lower limit on the bandwidth of the analogous bulk compounds, M₃C₆₀ if they exist. In particular, these experiments suggest that the measured dispersion for alkali fullerides should be larger for the LUMO derived t_{1u} band than that previously measured for the HOMO derived h_u band. Further experiments on epitaxial K₃C₆₀ are in progress to determine the bandwidth of this material. We are pleased to acknowledge the help of A. R. Kortan, A. V. Makhija and R. C. Haddon for preparing the C₆₀ material used in these experiments. We thank E. E. Chaban for constructing the C₆₀ evaporator used. We also acknowledge many useful discussions with our colleagues: D. R. Hamann and A. F. Hebard.

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Fermi Surface of a Quasi-One Dimensional Oxide Conductor.

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and Martha Greenblatt and William McCarroll, Department of Chemistry, Rutgers University.

The physical properties of quasi-one dimensional (1D) solids have been the subject of numerous investigations over many years. This interest originates in the fact that these materials allow fundamental theories of 1D systems to be directly tested. Transition metal oxide bronzes are a class of inorganic quasi-low dimensional solids that are ideal prototypical systems for spectroscopic studies due to the size and quality of available crystals. Among the unusual properties of these oxides are quasi-low dimensional electron transport, metal-insulator and metal-metal transitions, periodic lattice distortions and charge density wave transport. Interest in these oxides is further enhanced by the similarity of their properties to those of the high temperature oxide superconductors. A fundamental characteristic of one dimensional metals is the possibility of a Peierls transition in the metal lattice. This lattice instability is a direct consequence of the coupling between vibrational modes of the lattice and electrons at the Fermi level (E_F). Of particular importance in this coupling is the structure of the Fermi surface itself, since the degree of nesting and the density of states radically alters the magnitude of the anomaly in the generalized susceptibility that drives the lattice towards instability. Figure 1 presents the first measurement

Fig. 1. Measured Fermi surface for $\text{Li}_{0.9}\text{MoO}_{1.7}(001)$. $2k_F = 0.7 \pm 0.05 \text{ \AA}^{-1}$. $\bullet$ = data, $\triangle$ = symmetry points.

of a quasi-one dimensional Fermi surface in one of these oxides: $\text{Li}_{0.9}\text{MoO}_{1.7}$.¹ This material is metallic at room temperature, becomes insulating at 24K, and then superconducting at 1.9K. The Fermi surface of Fig. 1 was generated by using angle resolved photoemission to measure the dispersion of the Mo 4d states across E_F . The measurement was made at room temperature from samples cleaved in UHV. The measured Fermi surface consists of two parallel straight lines, with a nesting vector of $2k_F = 0.7 \text{ \AA}^{-1}$. The measurement allows us to predict the existence of significant phonon mode softening and/or a Peierls transition with a displacement vector of $q = 0.7 \text{ \AA}^{-1}$, and experiments are planned at Boston University using He atom scattering to search for these phenomena.

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Experimental Investigation of the X-ray Magnetic Circular Dichroism Sum-Rules

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Due to the difficulties associated with the commonly used total-electron- and fluorescence- yield x-ray absorption measurements, such as the saturation/self absorption effects and the influence on the electron detecting efficiency by an external magnetic field, the recently proposed x-ray magnetic circular dichroism (MCD) sum-rules [1,2] for deducing orbital and spin-magnetic moments has never been rigorously tested. To investigate the validity of the sum-rules and to provide a stringent test for all first principle x-ray MCD theoretical calculations, we have recorded the most reliable $L_{2,3}$ -edges MCD data for Fe, Co, and Ni transition metals (TM), using the transmission x-ray absorption technique and in-situ-grown thin films deposited on semi-transparent $1\mu\text{m}$ thick parylene windows.

To obtain XAS ($\sigma_+ + \sigma_-$) and MCD ($\sigma_+ - \sigma_-$) spectra for these thin films, transmission curves of TM+parylene and that of the parylene alone, taken with opposite magnetization directions, σ_+ and σ_- , were recorded. By dividing the photon-flux-normalized TM+parylene transmission data by that of the parylene and then taking their natural logarithm, one then obtains the σ_+ and σ_- absorption spectra of the TM. The figure shows the XAS, MCD, and the MCD integration of Fe, Co, and Ni. According to the sum-rules, the $\langle L_z \rangle$ to $\langle S_z \rangle$ ratio is related to the values of the "a" and "b" shown in the integration curves as $\langle L_z \rangle / \langle S_z \rangle = 4b / (9a - 6b)$. The ratios thus deduced are 0.086, 0.19, and 0.25 for Fe, Co, and Ni, respectively, showing a $\pm 30\%$ discrepancy as compare to the values of 0.124, 0.14, and 0.19, deduced from neutron scattering data. This inconsistency may be attributed to the uncertainty of the neutron results or the neglecting of multi-electron excitations in the derivation of the sum-rules.

Angular Dependence of Element Specific Magnetometry

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The intensity of the Magnetic Circular Dichroism (MCD) effect, which is the difference between the x-ray absorption of positive and negative helicity photons [1], is proportional to the projection of the elemental average moment along the photon propagation direction. We can measure the helicity dependent x-ray absorption spectra (XAS) in an applied magnetic field by a partial fluorescence yield method [2] and extract the element-resolved MCD intensity as a function of applied field (element specific magnetometry). Because of the flexibility of the measurement geometry, the analysis of the element specific magnetometry can be performed in an arbitrary direction with respect to an applied field to extract angular information concerning the magnetic behavior of a heteromagnetic multilayer. As an example, we have determined the relative Fe and Co magnetic moment directions of an Fe/Cu/Co trilayer film deposited on silicon by continuously rotating the analysis direction with respect to the applied field direction (as shown in the top panel) while monitoring the Fe and Co L_3 MCD intensities. The bottom panel shows the dependence of these intensities on the angle between the photon propagation and the applied field directions (azimuthal angle). The measured values are the data points with a fit to a cosine function [$M_0 \cos(\theta - \theta_0)$] as the solid line. It is clear from the data that the average Fe moment points along the applied field direction but the average Co moment is canted 20° from the applied field direction.

[1] C.T. Chen *et al.*, Phys. Rev. B **42**, 7262 (1990).

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Soft X-ray Magnetic Circular Dichroism of EuO Films

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We have used soft-x-ray magnetic circular dichroism (MCD), which is the difference between the x-ray absorption of positive and negative helicity photons at the 3d transition metal L_3 and L_2 and 4f rare-earth M_5 and M_4 absorption white lines [1], to examine the temperature dependent behavior of epitaxial EuO films deposited on sapphire and cubic zirconia substrates. The 50 Å EuO films, which are ferromagnetic insulators, were grown by thermal evaporation with the substrates held at 300°C , resulting in a nominally flat, single crystal film [2]. In the top panel of the figure at right is shown the x-ray absorption spectroscopy (XAS) spectra for negative-helicity (solid) and positive-helicity (dots) light at the Eu M_5 and M_4 absorption edge. The shoulder on the M_5 absorption feature (M_5^*) has the same helicity dependence as the M_4 absorption peak, and opposite the M_5 peak. This is consistent with the theoretical branching ratios for pure Eu [3] and is further confirmed in the temperature dependence of the M_5 and M_4 intensities shown in the bottom panel. The M_5/M_4 ratio is observed to be constant from room temperature down to $\sim 75^\circ\text{K}$, where a linear change in the ratio is observed. This break temperature is similar to the measured Curie temperature for the EuO film. The M_5^*/M_4 ratio is constant over the entire temperature range. The physical mechanism responsible for the linear behavior in the absorption peak ratio is not well understood.

[1] C.T. Chen *et al.*, Phys. Rev. B **42**, 7262 (1990).

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Dichroic Interference Effects in Circularly Polarized Soft-x-ray Resonant Magnetic Scattering

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By combining the high magnetic sensitivity of soft-x-ray magnetic circular dichroism and the structural sensitivity of the x-ray resonant scattering technique, we have demonstrated a new technique for probing interfacial magnetic structures: circularly polarized soft-x-ray resonant magnetic scattering. The left figure shows the Co $L_{2,3}$ -edges reflectivity of a magnetic multilayer thin film measured at a series of grazing angles, and with two opposite magnetization directions. The data show a maximum asymmetry ratio of 80%, greater than the degree of circular polarization of the incident light, and a changeover in the dichroic characteristics with increasing grazing angle. The right figure shows an inverted interference pattern in the angular dependence of the reflection asymmetry ratio at the L_3 white line. These intriguing observation are successfully explained by a model calculation based on classical electromagnetic theory. The complete polarization state of the incident light and the spatial interference within the multi-layers are found to be essential in achieving quantitative agreement with the measurements. This type of measurement has broad applications. For example, one can use it to study the interlayer spatial coupling of magnetic multilayers, to investigate the relationship between the interfacial magnetic roughness and giant magneto-resistance, or to serve as a high sensitivity polarimeter for characterizing the complete polarization of soft-x-rays.

Metal-Insulator Transition of V_2O_3

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$(V_{1-x}R_x)_2O_{3-y}$ ($R=Ti, Cr$) displays a complex phase diagram showing both metallic and insulating behavior, with and without antiferromagnetic ordering, with varying the temperature, pressure, x , and y . This system has attracted much attention, approximately 500 papers published in last 40 years, since it was considered a typical example of the Mott transition. However, this problem is not established yet.

We have studied the metal-insulator transition of $(V_{1-x}R_x)_2O_3$ ($R=Ti, Cr$) by using various electron spectroscopic techniques. Here we present, as an example, the high resolution valence band photoemission (PES), x-ray absorption (XAS) at the V 2p and O 1s edges, and resonant photoemission spectra (RESPES) at the V 2p edge. The sample is an annealed stoichiometric V_2O_3 single crystal. As can be seen in the figures, we observed the clear gap opening in the high resolution valence band PES at the insulating phase and spectral changes in all the spectra through the transition.

The spectroscopic data suggest that the oxygen $2p \rightarrow V3d$ charge transfer energy is much smaller than the previously expected value. Therefore, in order to understand the electronic structure and the phase transition of V_2O_3 , the hybridization between the V 3d and O 2p should be treated explicitly based on the many-body theory.

Spectroscopic Study of the Verwey transition of Fe_3O_4

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Magnetite, Fe_3O_4 , which is a mixed valence ferrite, undergoes a first order phase transition, so called the Verwey transition, at around 120K. At the transition, the electrical conductivity decreases by about two orders of magnitude, and this transition has been believed as a kind of metal-insulator transition even though the temperature dependence of the conductivity in the high temperature phase does not show the normal metallic behavior. Various models have been proposed to explain the transition and the anomaly in the conductivity behavior, but nothing is established yet. All proposed models assumed that there is a density of states at the Fermi level (E_F) in the high temperature (high T) phase. Surprisingly, it has not been proven by the high resolution electron spectroscopy measurement.

We have measured the high resolution valence band photoemission spectra from an annealed stoichiometric Fe_3O_4 single crystal above and below the transition temperature T_V . The used overall experimental resolutions are 80 and 60meV in the broad and in the near E_F spectra, respectively. As the results, we found that there is no emission at the E_F even in the high T phase. Through the transition, no significant spectral change was observed except in the region near the E_F , in which the ionization threshold is shifted by the order of 50meV to the low binding energy side at the high T phase. This shift, which means the decrease of the activation energy, is quite consistent with the conductivity increase by the two orders of magnitude at the transition. The sizes of the electrical gap above and below T_V are observed to be the order of 150 and 100meV, respectively, which are similar to the activation energies estimated from transport measurements.

Symmetry of hole states in p-type doped $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4\pm\delta}$

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Polarization-dependent x-ray-absorption spectroscopy measurements have been performed on the O1s-edges of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4\pm\delta}$ single crystals. From a comparison with recent data on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\delta}$ and NiO, we determine the energetic ordering of the states close to the Fermi level with $\text{Ni}(\text{Cu})3d_{x^2-y^2} / \text{O}2p_{x,y}$ orbital parentage on one side and $\text{Ni}(\text{Cu})3d_{3z^2-r^2} / \text{apex-O}2p_z$ orbital parentage on the other side for the undoped above compounds. This leads to strong disparities for the atomic and orbital character of the intrinsic and doped holes, indicating an enhanced out-of-plane character of the doped holes and a stronger in-plane hybridization between $\text{Ni}3d_{x^2-y^2}$ and $\text{O}2p_{x,y}$ orbitals in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4\pm\delta}$ compared to the respective coupling in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\delta}$. This is probably due to the different size of the Jahn-Teller distortion of the $\text{Ni}(\text{Cu})\text{O}_6$ octahedra, being strongest in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\delta}$, intermediate in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4\pm\delta}$, and which vanishes in NiO.

Polarization and doping-dependent O1s x-ray-absorption edges of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4\pm\delta}$ for the polarization vector of the linear polarized synchrotron radiation parallel (left) and perpendicular (right) to the NiO_2 planes. Solid: $x=0$, dotted: $x=0.1$, dot-dashed: $x=0.2$, dashed: $x=0.4$, dot-dot-dashed: $x=0.6$.

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U4B

Oxidation of potassium overlayers on graphite

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We have studied the oxidation of dispersed and metallic potassium overlayers on graphite by high resolution photoemission spectroscopy. The figures below show the evolution of the C1s core line as a function of oxygen exposure for a dispersed (left) and a metallic K(2x2) overlayer. All spectra were recorded in surface sensitive conditions. The C1s core line of clean graphite is plotted for comparison. The potassium overlayer causes the C1s line to shift to higher binding energy and induces a strong asymmetric broadening towards higher binding energies. Both effects are due to the charge transfer from the alkali to the graphite empty states at the Fermi level.

With oxygen exposure a charge redistribution occurs and shows up in a narrowing of the C1s line and a backshift towards lower binding energies. These results are in qualitative agreement with work recently published by Hock et al. (Phys. Rev. Lett. 71 (1993) 641), who suggest that oxygen pulls charge back out the surface graphite layer for dispersed phase. For the K(2x2) overlayer it appears that a more complicated process is occurring.

U4B

Soft X ray absorption of reduced and oxidized [2Fe-2S] protein.

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We have measured the Fe L edges of the [2Fe-2S] ferredoxin from *Clostridium pasteurianum*. This is a non heme protein which has, besides rubredoxin which contains one Fe atom, only two Fe atoms, in the oxidized form two Fe³⁺ ions and the reduced form one Fe²⁺ and one Fe³⁺ ion. The understanding of the electronic structure and magnetic coupling between the two Fe ions is important for the understanding of larger metalloproteins containing several [4Fe-4S], [3Fe-4S] or [2Fe-2S] clusters. In the figure we show the results of our measurements with the oxidized form at the top at half the absorption intensity. The ligand field atomic multiplet calculation is for a trivalent Fe ion in T_d symmetry with a ligand field splitting of 10Dq = -0.5 eV. The reduced spectrum (middle) is much broader and by subtracting the Fe³⁺ part we are able to analyze the Fe²⁺ spectral features. For the Fe²⁺ part (bottom) we find a 10Dq value of -0.6 eV. We used more reduced Slater integrals in the Fe³⁺ calculation (65% for the Fe²⁺ and 50% for the Fe³⁺), which shows that the Fe³⁺ site is more covalent. Clear from the data is that in the 2p absorption process the Fe²⁺ and Fe³⁺ ions in the reduced protein are probed individually. The energy separation is 600 meV between the Fe²⁺ and Fe³⁺ parts of the reduced protein, a value which is slightly smaller than found in the reduced and oxidized forms of rubredoxin (800 meV). The spectral features in the [2Fe-2S] from Cp are not as sharp as in rubredoxin which is most likely a result of a Fe-Fe interaction between the two sites. With the help of soft X-ray magnetic circular dichroism we will be able to study the magnetic coupling and the Zero Field Splittings (ZFS) of the individual Fe sites. A structural distortion from T_d symmetry splits the e_g orbitals, and for the Fe²⁺ ion the d_{z2} or d_{x2-y2} will be the only occupied minority spin orbital. The resulting ZFS has m_s=0 or m_s=±2 as ground state. A large soft X-ray MCD signal will arise with the m_s=±2 lowest state and a small or negligible soft X-ray MCD signal for the Fe²⁺ part will arise with the non degenerate m_s=0 ground state. The Fe³⁺ part of the reduced form should show the anti-ferromagnetic coupling to the Fe²⁺ site. The calculations with a D_{2d} symmetry show for the isotropic spectrum little difference upon a splitting of the 3d orbitals and an assignment can not be made without the soft X-ray MCD data. This protein is an electron transfer protein and it is important to know what the minority spin electron orbital is at the Fe²⁺ site, because it is this electron which is transferred in changing from the reduced to the oxidized form.

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Wavelength Dependent Transient Photoconductivity Decay in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$

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A technique is being developed for distinguishing the bulk and surface recombination rates of photogenerated carriers (electrons and holes) in semiconductors. The technique is based upon the standard transient photoconductivity decay method, where photocarriers are generated by a short pulse of light, and the recombination process is monitored electrically with an oscilloscope. A large surface recombination rate can be detected by comparing the initial decay rate for two conditions: one where the photocarriers are produced uniformly throughout the bulk of the material, and the other where the photocarriers are generated near the surface. The latter case will present a more rapid initial decay rate under conditions of large surface recombination. The variation of penetration depth with incident photon wavelength (energy) can be exploited for this purpose. Photons with energy well above the band gap experience a strong absorption coefficient and produce photocarriers within $1\ \mu\text{m}$ of the front surface. The absorption coefficient is much smaller for photon energies comparable to the bandgap, and photocarriers are produced more-or-less uniformly throughout the depth of a typical ($20\ \mu\text{m}$ thick) film. Infrared synchrotron radiation is a unique pulsed source which can be effectively tuned through the bandgap energy of most semiconductor materials. Using bandpass filters to vary the incident wavelength (and the photon energy), we have measured the photoconductivity decay for a $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ film under the two conditions described above, with the results shown in the figure at right. The $\tau=26\ \text{ns}$ decay time represents bulk recombination, whereas the shorter $\tau=14\ \text{ns}$ decay time indicates additional front surface recombination.

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Transient Photoresponse of a Long-Wavelength $\text{GaAs}/\text{Al}_{1-x}\text{Ga}_x\text{As}$ QWIP Detector

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Infrared detectors based on multiple layer, quantum well structures are promising candidates for applications requiring a combination of high speed and long-wavelength sensitivity. The spectral range of operation can be adjusted by varying the $\text{Al}_{1-x}\text{Ga}_x\text{As}$ x -value, well-width, and period. The speed of response is expected to be faster than $100\ \text{ps}$, and various techniques are being developed to demonstrate the performance of these detectors, including the response speed.

In this work we demonstrate the utility of pulsed infrared synchrotron radiation for characterizing the fast response of such quantum well infrared photodetectors (QWIPs). The VUV ring produces $\sim 500\ \text{ps}$ duration broadband infrared pulses which can be effectively tuned to match the spectral response of the device. Other advantages include high brightness and strong polarization that can facilitate coupling of the infrared into the QWIP structure.

The figure below shows initial results for a long wavelength ($9\ \mu\text{m} - 19\ \mu\text{m}$) QWIP. The linear dependence on bias indicates the absence of spurious photovoltages which might arise from electrical contacts. The fall time of a few nanoseconds is consistent with a $200\ \text{MHz}$ bandwidth pre-amplifier, and indicates a QWIP response of $< 1\ \text{ns}$. Faster electronics and electron bunch shortening will help to determine the intrinsic speed of these devices.

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U4IR

Dipole Forbidden Vibrational Modes for NO & CO on Cu in the Far-IR

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A breakdown of the dipole selection rule for adsorbate vibrational modes on metal surfaces is evident in the reflectance spectra reported below. The features at 285 cm^{-1} for CO and at 300 cm^{-1} for NO are dipole forbidden because they involve vibrations parallel to the metallic surfaces. The assignment was confirmed by isotopic substitution. They both have asymmetric lineshapes and are accompanied by an electronic broadband absorption. These observations are consistent with the non-adiabatic coupling of the vibrations with electronic transitions polarized parallel to the surface. NO has a different bonding configuration from CO: more highly coordinated than on-top, as inferred from EELS data. The figure shows a comparison between the reflectivity

spectra for a $(\sqrt{3} \times \sqrt{3})R30^\circ$ ($\theta=0.33$ monolayers) CO/Cu(111) and a $\theta=0.45$ monolayer coverage of NO/Cu(111). The striking similarities between the two spectra are the background slope and the appearance of an anti-absorption feature at 285 and 328 cm^{-1} respectively. One difference in the data is the appearance of a strong absorption peak for the carbon-metal stretch for CO, with no equivalent absorption for the NO. The CO data were taken at a resolution of 1 cm^{-1} , but for the NO data a resolution of 6 cm^{-1} was found to be adequate. This resolution difference is responsible for the lower noise in the NO data. Both sets of data were taken at 88 K , the

CO dose being 1.5 L and the NO dose 1.1 L . The NO coverage was chosen to maximize the 328 cm^{-1} mode.

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U4IR

Adsorbate-Induced Changes in the Infrared Reflectance of Cu(100)

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Using synchrotron radiation in conjunction with a photoconductive detector in the infrared region, we have established that the signal is strictly proportional to beam current over periods of at least 30 minutes to within an accuracy of $\pm 0.2\%$. We have used this to investigate CO on Cu(100) as a function of coverage, and in particular the broadband induced background changes which are predicted by the model of Persson¹.

The change in the reflectivity of a clean Cu(100) surface in uhr is shown as a function of CO coverage and frequency. Data were collected using two detectors - a photoconductive Cu doped Ge (liq. He cooled) above 400 cm^{-1} and a boron doped silicon bolometer (liq. He cooled) below 650 cm^{-1} . The solid lines are fits to the theory of Ref. 1. In addition, the strongest intramolecular vibrational mode is seen just above 2000 cm^{-1} , while the carbon-metal mode at 345 cm^{-1} and the hindered rotational mode at 286 cm^{-1} are only just visible on this scale. The asymptotic change at $\sim 2000\text{ cm}^{-1}$ is shown in the inset as a function of the coverage in monolayers.

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U4IR

High Resolution Far IR Vibrational Modes for CO on Cu(100), (111) and (110).

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Reflectivity spectra on electropolished samples of Cu(100), (111) and (110) with ordered overlayers of CO show much sharper features than in previous work on mechanically polished surfaces. In the figure we have plotted the change in the reflectivity compared to that of a clean surface, expressed as a percentage. The spectra

have been offset for clarity. The ordered overlayers are shown in cartoon form adjacent to the plots. The peaks at lower frequencies are due to the dipole forbidden hindered rotational mode, and the dips at higher frequencies due to the carbon-metal stretch. The background slope is due to changes in the electron scattering at the surface. The data is fitted (solid lines) to a Fano line-shape for the peaks and a Gaussian for the dips. The fits to these and the background can be compared to calculations for the background by Persson¹ and to the peaks themselves by Tully and Head-Gordon². In all cases a breakdown of the Born-Oppenheimer approximation appears to take place.

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- Work supported by US DOE Contract #DE-AC02-76CH00016.

NEW TECHNIQUES FOR STRUCTURAL STUDIES OF ADSORBED WATER

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We have recently expanded our capabilities for structural studies of adsorbed water with the addition of time-of-flight electron stimulated desorption ion angular distributions (TOF-ESDIAD) and fourier transform far-infrared spectroscopy (far-FTIR) using a synchrotron radiation source. TOF-ESDIAD allows the extraction of orientational information in the presence of interfering species such as O, F, and Cl, which have high cross sections for ion production, and which are of interest in surface science models of the electrochemical environment. Far-FTIR provides molecular identification and bonding information of adsorbates and is suitable for both the metal/vacuum and metal/liquid interfaces. We will present TOF-ESDIAD results for the H₂O/F/Ag(110) coadsorption system that show an unusual orientation for water in the presence of surface fluorine, that could not have been determined without mass resolution. We will describe preliminary far-FTIR measurements of H₂O adsorbed on the clean and oxygen-covered Ag(110) surfaces and compare them to previous studies by high resolution electron energy loss spectroscopy and similar work done at this facility in electrochemical cells.

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ROTATIONAL PHASE TRANSITION IN THE FAR-IR TRANSMISSION OF THICK C_{60} SINGLE CRYSTALS

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We report the measurement of the far-infrared transmission of large C_{60} single crystals. Spectra of thin film C_{60} show the four F_{1u} vibrational modes allowed by symmetry¹. But when our crystals are thick enough, the spectra exhibit a very rich structure with over 120 vibrational absorptions visible in the 100 - 4000 cm^{-1} range. We observe silent modes becoming weakly IR-active, probably due to isotopic impurities breaking the icosahedral I_h symmetry of the pure C_{60} molecule. In the far-IR we observe new vibrational modes at 342, 353, 403, 431, and 485 cm^{-1} in addition to the two F_{1u} modes at 526 and 576 cm^{-1} .

The figure shows how the far-IR spectra changes with temperature as we move through the rotational phase transition at $T_c \sim 250K$. Clearly all of the vibrational modes observed in this region narrow considerably below T_c . This is understood from knowing that the C_{60} molecules stop freely spinning and lock into one of two configurations. The higher symmetry of frozen molecules results in much less broadening of any vibration. Indeed the modes show no further narrowing down to 77K. We observe very similar behavior in the mid-IR vibrational modes measured on the same crystals at beamline U2B².

The U4IR beamline allowed us to measure our C_{60} crystals in the far-IR, completing the entire IR region where intramolecular modes in C_{60} and their higher order combinations exist. The combination of both mid- and far-IR spectra over a range of temperatures greatly aided our effort to determine the large number of weak modes' symmetry assignments. By carefully analyzing the higher order vibrations and using group theory considerations, we assigned candidate frequencies for the F_{1g} vibrations and to the F_{2u} , G_u , H_u group of odd-parity vibrations³.

This work is supported by NSF Grant DMR 9202528.

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3. Michael C. Martin, Xiaogun Du, and L. Mihaly *to be published*.

SYNCHROTRON INFRARED SPECTROSCOPY OF H_2O AND ADSORBES AT THE ELECTROCHEMICAL INTERFACE*

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The far infrared spectra of H_2O adsorbed on Pt(III) single crystal at UHV were measured for the first time as a function of temperature and coverage. A typical result at 101°K and low exposure is shown in Fig. 1. The broad band centered at about 240 cm^{-1} is attributed to the hindered translation of the water molecules on the Pt. surface. The spectrum is very similar to what we have observed for H_2O adsorbed on polycrystalline Au¹⁾. As in the case with Au, water is adsorbed molecularly and non-dissociatively on the Pt(III) surface.^{2,3)}

We have also successfully carried out initial experiments to study the structure of adsorbates at the electrode/solution interface as a function of an applied electrical potential. Preliminary results have been obtained on CO and SCN⁻ adsorbed on Pt. in aqueous HClO₄ and NaClO₄ solutions, respectively.

Fig. 1. Far IR spectra of H_2O adsorbed on Pt(III) at 101°K. (B, background; L, exposure in Langmuirs).

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In Situ Far-infrared Evidence for a Potential Dependence of Silver-Water Interactions

Andrea E. Russell (University of Liverpool, U.K.), Andrew S. Lin and William E. O'Grady (Naval Research Laboratory, U.S.A.) Published in Faraday Trans., **89** (1993) 195

The influence of the adsorption of fluoride on the bonding of water to a silver electrode surface was studied by observing the $\nu(\text{Ag-O})$ stretching vibration in the far-infrared. The experiments were conducted using potential difference external reflectance spectroscopy with synchrotron radiation as the far-infrared source. It was found that the adsorption of fluoride ions at potentials positive of the pzc decreased the coverage of water adsorbed on the silver electrode surface. At potentials negative of the pzc water molecules were found to be bound to the silver surface through the oxygen atom.

The spectra shown in figure 1 illustrates the effect of making the potential more negative on the adsorption of water on Ag(111) in 0.1 mol dm⁻³ NaF. One upward pointing band at 322 cm⁻¹ is observed. The direction of the band indicates that the species responsible is present in a greater concentration/coverage at the reference potential, -1.0 V vs. SCE. The pzc of Ag(111) is -0.695 V as stated above. Therefore, the band is unlikely to be associated with an anionic adsorbate. The band is assigned to the $\nu(\text{Ag-O})$ stretching vibration of adsorbed/bound water based on comparison to UHV EELS (electron energy loss spectroscopy) measurements of water adsorption on Ag(110). In the EELS studies the $\nu(\text{Ag-O})$ stretching vibration of adsorbed water and OH were reported at 320 or 280 cm⁻¹, respectively.

Difference spectra for Ag(111) in 0.1 mol dm⁻³ NaF. Reference potential is -1.0 V vs. SCE. Sample potentials as in figure.

As seen in the figure, the intensity of the upward pointing band decreases as the sample potential is made more negative until the sample potential is -0.7 V vs. SCE and continuing down to -1.1 V. Below -0.7 V, the sample and reference spectra are enough alike that the band at 322 cm⁻¹ is barely visible. Upon returning to more positive potentials the band at 322 cm⁻¹ is observed to reappear at sample potentials as negative as -1.0 V vs. SCE. The intensity of the band then continues to increase as the sample potential is made increasingly positive. These results indicate that the coverage of water on the silver surface is greater at the reference potential, -1.0 V than at the sample potentials more positive than -0.7 V, which is approximately the pzc.

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Far-infrared synchrotron radiation for in situ studies of the electrochemical interface

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This paper represents the first application of far-infrared radiation from a synchrotron source to the study of the electrode/electrolyte interface in situ. The increased brightness offered by synchrotron radiation over conventional far-infrared sources makes the extension of in situ reflectance measurements to the far-infrared realistically feasible. The coupling efficiency between the source and sample is increased from 8×10^{-4} for a 2000 °K black body source to 1 with the synchrotron source. Thus, the acquisition times per spectrum are reduced from on the order of an hour to less than ten minutes.

In this first study, the adsorption of perchlorate and chloride ions on Ag(111) was investigated. The spectrum shown in the figure was obtained for a Ag(111) single crystal electrode in 0.1 mol dm⁻³ HClO₄. The reference spectrum, at -0.3 V vs. SCE, was collected at the beginning of the potential sequence. Sample spectra were then collected during several potential excursions from -0.3 to -0.65 V vs. SCE and back. The regular, sharp, narrow features in the spectra may be attributed to fluctuations in the water vapour in the path of the IR radiation. The band centered at 190 cm⁻¹ is attributed to the formation of adsorbed chloride from the slow reduction of perchlorate in the hydrogen evolution region by an ec mechanism.

Difference spectra obtained after second cathodic excursion. Sample potential is -0.65 V vs. SCE.

The frequency of the $\nu(\text{Ag-Cl})$ stretching vibration observed in this experiment, 190 cm⁻¹, may then be compared to that obtained by various SERS studies; the $\nu(\text{Ag-Cl})$ band ranges between 215 and 240 cm⁻¹. The discrepancy between the SERS results and those obtained in this infrared reflectance experiment may be attributed to the difference in coverage of adsorbed chloride in the two experiments. Dipolar interactions between adjacent adsorbates can result in a shift in the vibrational frequencies of the adsorbed molecules. The dipole term arises from the dipole formed by the adsorbed ion and the corresponding image charge within the metal. Such terms do not become appreciable until chloride coverages of 2/3 of a monolayer are reached. The 190 cm⁻¹ band reported for adsorbed chloride species observed from the reduction of perchlorate in this *in situ* far-infrared study is, therefore, attributed to coverages below 2/3 of a monolayer.

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IMPERFECT FERROMAGNETIC COUPLING OF THE Gd(0001) SURFACE

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Properties of magnetic surfaces and anisotropy between surface and bulk magnetic systems have been of considerable interest. Previous experiments on Gd(0001) have shown enhanced surface magnetic order¹ and theoretical calculations² have predicted an antiferromagnetic coupling between the bulk and surface. However, our study shows conclusively that the surface is predominantly ferromagnetically coupled to the bulk, consistent with previous experiments³.

The figure shows the spin polarized spectrum of the Gd 4f levels taken at 46eV incident photon energy. The binding energy of the surface component is $0.37 \pm 0.2\text{eV}$ greater than the bulk. Both these 4f levels are strongly polarized in the same direction, indicating significant ferromagnetic coupling. However, further examination of the magnetization of the surface and bulk 4f levels indicates an imperfect coupling between the bulk and surface magnetic structure. The different contributions of the surface layer and bulk contributions to the polarization spectrum can readily be seen in the figure. We hypothesize that the origin of this difference results from the existence of a perpendicular component of the surface magnetization, which is reflected by a reduction in the parallel component of the magnetization. Earlier experiments examining the secondary electron yield have observed a perpendicular component in the background polarization⁴. Furthermore, we note that this perpendicular component is very sensitive to contamination. A slight contamination of the surface results in significant reduction in this component, as is evidenced in the more perfectly ferromagnetic coupling of the Gd(0001) films of reference 3.

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DIELECTRIC THIN FILM DEPOSITION FROM CONDENSED REACTANTS BY ULTRAVIOLET AND SOFT X-RAY IRRADIATION.

U7a

J.F. Moore, D.R. Strongin (SUNY at Stony Brook)
M. Strongin and M.W. Ruckman (BNL Physics)

A novel method for the deposition of alumina, silica, silicon carbide, and boron nitride at temperatures below 100 K is being developed. The technique involves *condensing* a reactive mixture of gases onto the cooled substrate, followed by an exposure to the zero order beam (150- 650 eV). The condensate is selectively converted to a pure, refractory solid, while unreacted material or volatile products are desorbed during the reaction or on warming to ambient conditions. Characterization of the process has been carried out using photoelectron spectroscopy, near-edge x-ray absorption, auger electron spectroscopy, and mass spectrometry. We have also done comparative studies using a pulsed UV laser (4.6 eV) as the excitation source.

Results suggest that the growth induced by soft x-rays is excited by secondary electrons, self-limiting the thickness to below 50 Å. In contrast, the laser-stimulated growth can generate films which are greater than 100 Å in thickness, and appears to occur by *direct* absorption of photons in the condensed film. In figure 1, the change in XPS peak positions and intensities can be followed through the processing stages for a case of silica film growth. The curves represent: a) the condensed mixture of tetramethylsilane and water b) after exposure to the white beam and c) after warming to room temperature. Note the dramatic drop in carbon intensity, indicating desorption as a volatile product. The progression of the O K-edge NEXAFS is shown similarly in figure 2.

Current work is aimed at understanding the mechanism of growth by observing photoion yield as a function of photon energy.

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Adsorption of Deuterium and Hydrogen on Cu films grown at Liquid Helium Temperature

M. W. Ruckman, F. M. Jacobsen, S. Woronick, J. F. Moore and Myron Strongin (BNL-Physics)

A central problem in surface science is adsorption of molecules on metal surfaces. There is much speculation about the physical mechanisms involved and nature of adsorbed molecular species. Much of the confusion could be cleared up by studying the adsorption of cold molecular species on surfaces cooled to liquid helium temperature.

We are studying the interaction of hydrogen and its isotopes with copper at 4-5 K because of the relative simplicity of the system and its relevance to the vacuum performance of the SSC. The binding of hydrogen to surfaces and the rate of photon-assisted desorption governs the vacuum pressure in the SSC which is operated with a liquid helium cooled beam pipe. Fundamental data concerning the sticking of hydrogen to polycrystalline Cu surfaces is lacking.

Figure 1 shows the attenuation of the Cu 3d states during D₂ adsorption on a clean Cu film at 5 K. It is known that deuterium dissociates on Cu surfaces and physisorbs on Cu surfaces cooled below 8 K. The curve shows that the D₂ has a relatively high sticking coefficient during the first stage of D₂ adsorption and also shows an abrupt decrease in the D₂ uptake that corresponds to a transition from one adsorption state to another.

The photoemission from D₂/Cu is shown from Fig. 2. The initial stage of D₂ adsorption generates a species that attenuates the Cu 3d band as shown in Fig. 1 and generates a loss edge starting near 15 eV binding energy. Measurable photoemission from the D₂ 1σ_g is not seen until the rate of D₂ adsorption decreases (i.e. the knee in the curve in Fig. 1) and solid D₂ begins to build-up on the surface. The existence of the loss feature argues for molecular D₂ adsorption but the failure to observe the primary photoelectron peak is a mystery.

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Photoelectron and Near-edge Studies of the Reaction of NH₃ with Potassium at Liquid Helium Temperatures

Bo Xia, M. W. Ruckman and Myron Strongin (BNL-Physics)

Photoelectron and near-edge spectroscopies were used to characterize the low temperature chemical behavior of potassium when put into solid NH₃ cooled to less than 10 K and when NH₃ is put on a potassium film at the same temperature. This was done because the adsorption of NH₃ on discontinuous potassium films causes non-reversible changes in the conductivity when the films are annealed at cryogenic temperatures and there was a need to determine whether the changes were chemical or physical in nature. The accompanying figures show a typical experiment in which NH₃ is condensed on a thick potassium film grown on a silver covered copper plate at 7 K.

Figure 1 shows valence band photoemission for the clean potassium film, the same film after exposure to 3 L of NH₃ and that surface after raising the temperature to 25 and 50 K, respectively. Figures 2 and 3 show similar data for the N 1s core level and N K-edge. The EDC for the clean potassium film shows the K 3p peak and associated plasmon-loss peaks. The plasmon peaks are quenched when the NH₃ is put on the surface and three new peaks associated with NH₃ are seen. The core level and near-edge data match those of thick NH₃ films showing that the NH₃ is intact on the surface at 7 K. Upon heating to 25 K, new features are seen in all the spectra (marked by a vertical line). All of the features can be associated with the solid N₂ which is retained on surfaces at 25 K. The N₂-related features disappear when the NH₃-K system is heated to 50 K. This is as expected given the vapor pressure of solid N₂ at 50 K.

The experiment demonstrates that potassium and NH₃ react near 20 K to form products including N₂. The hydrogen liberated by this reaction may escape or bond to the potassium to form a hydride. The observed reaction is clearly unfavorable from the stand point of chemical kinetics. Control experiments were done to eliminate photon-assisted processes as a source of the reaction and we feel that an electro-chemical or quantum mechanical process may account for the NH₃ bond breaking.

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U7b

Photoelectron Studies of Iron and Palladium Cluster Growth on a Fullerene Film

M. W. Ruckman (BNL-Physics), David Shih (BNL-SERS) and Bo Xia (BNL-Physics)

Techniques like photoelectron spectroscopy have been used to study nano-sized metal clusters. Clusters for these experiments have been produced by matrix-isolation or growth on surfaces like graphite. Control of the cluster size is more art than science and in many cases small clusters can only be grown for low surface concentration because the best supports for cluster growth like exfoliated graphite have high rates of surface diffusion. Rare gases like Xe or Kr are good matrices for growing small clusters but limit the thermal ranges studied to those in which the matrix is stable. As the work described will show, fullerenes can be used in some cases to isolate and grow metal clusters at room temperature for a variety of chemisorption studies.

Pd and Fe clusters were grown on fullerene films by physical vapor deposition. The fullerenes themselves were sublimed from a commercial fullerene powder (80% C_{60} / 20 % C_{70}). Figure 1 shows results for the growth of Pd clusters in the C_{60} dominated matrix. Figure 2 shows the same result for iron. We conclude that Pd forms clusters in C_{60} by comparing the data to Pd isolated in Xe [1]. Small Pd clusters have the d^{10} configuration and show (1) few, if any, states at the Fermi edge, (2) a narrow d-band and (3) a shift of the d-band centroid away from E_F . All three were observed for Pd isolated in C_{60} and the data matched the result seen for Pd isolated in Xe. Similar results were seen for iron (Figure 2). Calculations for iron clusters show that clusters with fewer than 9 atoms have a small density of states at the Fermi edge. An examination of the Fe 3p core level revealed that the modification of the valence states can not be attributed to oxidation because the core level components normally seen for divalent or trivalent iron species are absent.

Some preliminary experiments were done in which the Pd clusters were exposed to hydrogen and oxygen. Small Pd clusters proved to be somewhat inert while clusters large enough to produce states at the Fermi edge could bond hydrogen or oxygen.

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U7b

Photoelectron and Near-edge X-ray Absorption Fine Structure Studies of Al, TiAl, FeAl and NiAl

D. R. Strongin, N. R. Gleason, B. R. Sheu (SUNY-Stony Brook-Chemistry) and M. W. Ruckman (BNL-Physics)

Transition metal Aluminides have great potential as structural materials due to their high strength to weight ratios and ability to form a protective Al_2O_3 skin at high temperatures in hostile environments. However, their lack of ductility at room temperature is a major barrier to their wide spread use. Much research is now focused on this ductility problem and a major thrust is the determination of their electronic structure and characterizing their reactivity towards various adsorbates to isolate environmental embrittlements and/or find new ways to passivate their surfaces. The research presented here uses synchrotron radiation to study the electronic structure of three aluminides that span the first transition metal series: TiAl, FeAl and NiAl. Fig. 1 shows the valence band states of the aluminides, all of which show a reduced density of states at the Fermi level (E_F) compared to the corresponding pure transition metals. The NiAl d-band is shifted to higher binding energy, about 2 eV below E_F , and calculations show that the d-band is filled. The d-bands of TiAl and FeAl reside at E_F , and calculations show that their d-bands are unfilled. Near-edge spectra of metals reflect the density of states in the region above E_F . Fig. 2 shows the near-edge spectra for Al and the aluminides. It can be seen in the spectra that the Al L-edge occurs at a photon energy of 73 eV. TiAl and FeAl show absorption at that photon energy, although the intensity is reduced compared to pure Al. The TiAl and FeAl spectra also contain a second absorption edge at 75.5 eV. The NiAl spectrum has only one absorption edge at 75.5 eV. The data suggests the feature at 73 eV is due to a transition to unoccupied Al states hybridized with Ti or Fe 3d states at the Fermi edge, while the feature at 75.5 eV (absent in pure Al) is due to states shifted above E_F . All of the aluminides have such a feature in their valence bands.

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PHOTON-STIMULATED DESORPTION OF F⁺ FROM CaF₂ GROWN ON Si(111)

U8A

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CaF₂ is a technologically important material, with applications in electronic device technology and optics. High quality CaF₂ films can be grown *in situ* via molecular beam epitaxy. CaF₂ as well as other metal halide systems, however, are very susceptible to radiation damage. When irradiated with electrons or photons of sufficient energy, F-center defects are easily formed which, in turn, alter the electrical and optical properties. In the case of CaF₂, formation of F-centers result from the replacement of F⁻ anion with an electron. In the present study, photon-stimulated desorption (PSD) of F⁺ ions is used to identify the electronic transitions responsible for F-center formation in CaF₂.

A PSD spectrum from a CaF₂ is shown in the figure. The films were grown on Si(111) substrates and the ions were collected over all energies and over all angles. The expected energies for the onset of various electronic transitions responsible for F⁺ PSD, determined from photoemission, are also shown in the figure. Double ionization of F⁻, which leads to the desorption of F⁺ ions, can occur via core ionization of F⁻ followed by an *intra*-atomic Auger decay or core ionization of the Ca²⁺ followed by an *inter*-atomic Auger decay. Both processes would leave the Ca-F complex in the Ca²⁺.F⁺ repulsive state. The data show that the PSD of F⁺ ions occurs following the creation of a core hole at the Ca 3p level. Excitation of the F 2s core level, on the other hand, does not lead to F⁺ desorption. This difference is not due to the lack of photon absorption at the F 2s core level, as total electron yield (TEY) spectra from these films, also shown in the figure, indicate that photons are absorbed at the F 2s edge. These results clearly demonstrate that the repulsive final states that result from the excitations of anion (F⁻) and cation (Ca²⁺) core levels are different. It is proposed that the observed difference in the repulsive final states arises from different lifetimes of anion and cation core holes in conjunction with nuclear motion prior to the Auger decay.

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PHOTON-STIMULATED DESORPTION OF Cl⁺ FROM Si

U8A

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Stimulated desorption of positive ions from surfaces is commonly used to investigate the local electronic structure and bonding geometries of adsorbates. The mechanisms for these processes are often complex, however, as they depend on both the initial and final state configurations of multi-component systems. Since photon stimulated desorption (PSD) directly probes the transitions that give rise to stimulated desorption, it is an ideal technique for delineating these mechanisms. In this study, PSD of Cl⁺ from Si is studied with photon energies in the regions of the Si 2p and Cl 3s core-levels. At the Si 2p edge, the onset of PSD occurs at the same energy as the bulk absorption edge, as shown in the top figure. This indicates that PSD at the Si 2p edge occurs via an indirect process in which secondary electrons induce ESD by directly exciting a lower energy transition. This transition is from the Cl 3s core-level to Cl antibonding levels which are known to exist at ~6.5 eV above the valence band maximum. The onset for this transition is at ~20 eV, as shown in the bottom figure.

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GaF₃ FILM GROWTH ON GaAs WAFERS STUDIED BY SOFT X-RAY PHOTOEMISSION

U8A

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The fluorination of GaAs wafers by XeF₂ is studied using soft x-ray photoemission spectroscopy (SXPS). This reaction provides a simple chemical process for growing GaF₃, a 9.6 eV band-gap insulator, on a GaAs substrate. In order for a GaF₃/GaAs structure to be practical in a microelectronic device, however, it must have a very low interface state density. This work focuses on how the interface quality is affected by the temperature of the substrate during film growth. SXPS spectra allow for a quantitative determination of the composition of the interface, which is comprised of AsF, GaF, and trivalent As and Ga atoms.

The figure below shows total film composition, given as thickness in Å, for seven different substrate temperatures at a fixed exposure of 10 kL (1 kL=10⁻³ torr-sec). The monofluorides are shown separately for illustration purposes only, and are not actually segregated in this manner. From 300 K to the sublimation temperature of GaF₃ (~600 K) the interface thickness is essentially unchanged. For temperatures of 600 K and above, the reaction changes from GaF₃ film growth to complete etching, since all reaction products are volatile at these temperatures.

PHOTON-STIMULATED DESORPTION STUDIES of GaF₃ FILM GROWTH ON GaAs WAFERS

U8A

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GaAs wafers were reacted with XeF₂, which produced films of solid GaF₃. The films were studied using photon-stimulated desorption (PSD), which is extremely surface sensitive due to the small mean-free-path of F⁺. The mechanism responsible for F⁺ PSD begins with the photoionization of a core electron, followed by an Auger decay that fills the core hole from the electron-rich GaF₃ valence band, which has mostly F 2p character. The resulting F⁺ ion is then ejected from the surface by Coulombic repulsion. PSD spectra collected after the initial XeF₂ exposures contain a single feature, whereas PSD spectra collected after larger exposures contain features due to transitions within the GaF₃ band structure, thus providing the absorption spectra of solid GaF₃. The change in the PSD spectra occurs for a film thickness between 5 Å and 10 Å, which signals the onset of the bulk GaF₃ electronic structure.

The figure below shows representative PSD spectra. For low exposures, the single PSD feature at ~35 eV is due to the excitation of a F 2s electron to the GaAs conduction band minimum (CBM). For higher exposures, the large feature between 30 and 38 eV and the one at ~40 eV are most likely due to Ga 3d transitions, while the feature at ~52 eV is due to a F 2s transition.

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THE CHEMICAL VAPOR DEPOSITION OF TRICHLOROMETHYLSILANE ON Si(111)

D. A. Lapiano-Smith, L. J. Terminello (LLNL) and F. J. Himself (IBM)

Soft x-ray photoemission spectroscopy has been used to investigate the chemisorption and reaction of SiCl_3CH_3 on Si(111) and (100) surfaces as part of the SiC atomic layer epitaxy (ALE) project. To date, we have only examined the interaction of alkylsilanes on Si surfaces. The reaction of SiCl_3CH_3 on the technologically important Si(100) surface was examined initially. We have found that replacing H in the molecular precursor by the more strongly bound Cl, as in SiCl_3CH_3 , causes the molecule to become so inert that a significant OH contamination of the (100) surface occurred before completing a monolayer coverage. The results obtained following the exposure of Si(111) to SiCl_3CH_3 are discussed below. This surface is much less reactive towards OH contamination than the Si(100).

A series of valence band spectra are shown in the figure below. The spectrum shown in panel a is characteristic of a clean Si(111) surface. The spectrum shown in panel b results following an exposure of the Si(111) surface to 6000L SiCl_3CH_3 at room temperature. This spectrum shows clearly that very little carbon chemisorption results following the decomposition of SiCl_3CH_3 . This observation is in contrast to that observed previously for the reaction of alkylsilanes with Si. In addition, it is difficult to determine an approximate C 2s intensity contribution to the peak at about 34 eV kinetic energy, since the Cl 3s photoemission signal overlaps in this region. The spectrum in panel c results following an anneal of the prepared surface to 500°C. While a significant decrease of surface species has occurred it is assumed that -CH₃ and Cl species remain on the surface. The investigation of dimethylsilane/Si has shown that methyl groups are stable on the surface at 500°C. In addition, Cl is known to remain on Si surfaces to temperatures above 800°C. From this exploratory experiment we conclude that a useful compound for SiC ALE must contain H ligands, rather than Cl, in order to facilitate C chemisorption.

THE CHEMISORPTION AND REACTION OF DIMETHYLSILANE ON Si(111)

D. A. Lapiano-Smith, L. J. Terminello (LLNL) and F. J. Himself (IBM)

The main objective of this project has been to identify the chemical species that are present on a Si semiconductor surface following the chemical vapor deposition of an alkylsilane as a function of substrate temperature. In addition, we intend to determine whether the chosen molecular precursor is suitable for Si atomic layer epitaxy (ALE) or has greater potential for SiC ALE. In order to obtain criteria for the use of various compounds in SiC ALE, the ligands of the alkylsilanes have been varied systematically in the course of this work.

The surface chemistry involved in the chemisorption and thermal reaction of dimethylsilane (DMS) on Si(111) has been examined for growth at room temperature and subsequent annealing as well as for growth at elevated temperatures. Soft x-ray photoemission spectroscopy has been used as the surface-sensitive technique to probe the shallow C 2s core level in the valence band and the C 1s and Si 2p core levels. We have found that DMS chemisorbs dissociatively to form Si-CH₃ surface species on Si(111) at room temperature. Likewise, -CH₂CH₃ groups saturate the surface when using diethylsilane (1). These different alkyl species can be distinguished very nicely at the surface by the splitting of the C 2s level, which gives directly the number of C atoms in the alkyl group. The figure below shows the valence band spectrum characteristic of a clean Si(111) surface as the dashed line. The spectrum depicted as the solid line represents a saturation coverage of the (111) surface following its exposure to 2500L DMS at room temperature. The very sharp, single peak at about 35 eV kinetic energy serves to "fingerprint" the identification of chemisorbed -CH₃ (methyl) groups on the surface. An anneal of the surface to 500°C promotes the onset of desorption of the methyl groups from the surface. Although decreasing in intensity, the CH₃ species continue to persist until a temperature of about 580°C is attained. At this temperature, the remaining methyl species dissociate to form Si-C surface species.

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Fluorescence Lifetime Measurements in Crude Oils

Oliver C. Mullins, Schlumberger-Doll Research and Xin Wang, U. C., Davis

The fluorescence properties of crude oils and other natural materials are utilized in a variety of commercial applications, such as remote detection of potential oil fields, source rock evaluation and oil detection during drilling. The fluorescence spectra of crude oils have been the subject of numerous studies in the literature primarily through standard steady state methods. In our general effort to better characterize the fluorescence properties of crude oils, we have undertaken a study of the fluorescence lifetime characteristics of crude oils. Generally, the fluorescence lifetimes of dilute solutions of crude oils can be accurately described as consisting of two components, each with appreciable population. The long component varies from 40 nanoseconds (ns) at short wavelength emission to 10 ns with long wave emission. Combining the lifetime studies with studies of fluorescence spectra and relative quantum yields as a function of the crude oil type and concentration yields a cohesive picture of the energy transfer process. For intermediate concentrations of crude oil solutions, the lifetime for short wavelength emission decreases much more rapidly than the lifetime for long wavelength emission. Small, organic chromophores with a large bandgap collisionally transfer energy to larger chromophores with a smaller bandgap. This additional decay channel for the more concentrated solutions of crude oils results in the large decrease in the fluorescence lifetime for short wavelength emission. However, for these intermediate concentrations, the long wavelength emission is not strongly affected because the crude oils are relatively dilute in the large chromophores. Finally, for very concentrated solutions, all lifetimes drop to very small values independent of wavelength, due to collisional quenching.

RELATIONSHIP BETWEEN LIFETIME AND CONCENTRATION OF FITC

Suzanne Scarlata and Loren Runnels (SUNY Stony Brook)

The purpose of these experiments was to measure the concentration dependence of fluorescence lifetimes and anisotropy decays of varying concentrations of fluorescein isothiocyanate (FITC) in 100% glycerol. By steady state methods we have found that increasing fluorescein concentrations produces a systematic decrease in observed anisotropy (independent of the effects of concentrational quenching). This decrease can be attributed to energy transfer between fluorescein molecules. The closer the neighboring fluorescein molecules, the greater the probability for energy transfer. The process of energy transfer between fluorophores will cause the emitted photons to change their polarization as they pass from one probe to the next. This process should also result in a net increase in fluorescence lifetime. On a previous visit to BNL, we measured the concentration dependence of the fluorescence lifetime of FITC in 80% glycerol and observed an increase in fluorescent lifetime for a systematic increase in concentration. We similarly measured the concentration dependence of the fluorescence lifetime of fluorescein-labelled phosphatidylethanolamine incorporated into either multilamellar or unilamellar dioleoylphosphatidylcholine vesicles, but saw a decrease in fluorescence lifetime when the fluorescein-labeled lipid to unlabeled lipid molar ratio was increased. On this visit, our aim was to illuminate the seeming disparity between the two series of previous measurements by extending the concentration range of the FITC in glycerol so that the virtual separation distance between fluorophores in glycerol were similar to that calculated for fluorescein-labelled lipids incorporated into lipid vesicles. Our results are shown in the figure below. With decreasing separation radius (increasing concentration) the fluorescent lifetime gradually increases to a peak, and then falls off rapidly as the separation radius approaches zero. The new data agrees with both the previous measurements, and suggests the presence of a concentrational quenching effect -- later confirmed by steady state techniques. The new data, when coupled with steady state measurements, indicates that energy transfer does occur within the lifetimes observed. We are presently incorporating the data obtained from the anisotropy decays into various models which should reveal more detail about the phenomenon of energy transfer.

U9B

SECONDARY STRUCTURE ANALYSIS OF THE CASTOR STEAROYL-ACP DESATURASE

J. Shanklin (BNL) and L. France (USDA, Plum Island)

We are in the process of understanding the mechanism of action of the plant stearyl-ACP desaturase, an enzyme that introduces the first double bond into saturated acyl chains. It possesses a binuclear iron cluster similar to that seen in a central four helix bundle within ribonucleotide reductase. We tested the hypothesis that the desaturase also possesses a four helix bundle by performing secondary structure analysis using CD spectroscopy, to determine if it possesses sufficient α helix to form such a structure.

As seen below, the desaturase contains a very high proportion of α helix (76 percent), a result consistent with the proposed model. The detailed structure of the desaturase is currently being solved using X-ray crystallography.

Structure	α -helix	antiparallel β -sheet	parallel β -sheet	β -turns (all types)	Other	Total
DES	0.76	0.00	0.03	0.10	0.12	1.01

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VACUUM UV CIRCULAR DICHROISM OF POLYSACCHARIDES

U9B

E. S. Stevens (SUNY Binghamton)

Continuing our program of determining polysaccharide conformations from vacuum UV circular dichroism (CD) measurements, we have measured the CD of agarose films prepared under a variety of conditions. The purpose of the project has been to attempt to distinguish between "double-helix" and "single-helix" models of agarose gelation.

Motivation for the CD project comes from reports that agarose films prepared by drying 100° C solutions, cooling to room temperature, and stretching at 50° C (or above) (i.e., "HT films") give "crystalline" x-ray diffraction patterns interpretable in terms of single extended chains. Films prepared entirely at room temperature ("RT films") give "diffuse" x-ray diffraction patterns, only marginally interpretable, but previously assigned to intertwined double helices. The HT film diffraction pattern raises the possibility that the RT films also contain single helices.

The CD of the HT and RT films, however, are distinctly different, particularly with respect to the wavelength of a positive CD band which occurs near 178 nm in RT films and 185 nm in HT films. This distinction is the same as occurs in non-film samples, between the gel form (178 nm) and sol form (185 nm). Thus, preparation of HT films provides no avenue to achieve the structuring present in RT films, and the presence of single-helices in stretched HT films does not have a bearing on the conformation of the chains in RT gels and RT films.

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DECAY KINETICS OF THE $\text{Gd}_2(\text{SiO}_4)\text{O}:\text{Ce}$ SCINTILLATOR

H. Suzuki and T.A. Tombrello (Caltech), C.L. Melcher and J. S. Schweitzer (Schlumberger)

It is our purpose to understand the scintillation mechanism of Ce-doped gadolinium oxyorthosilicate $\text{Gd}_2(\text{SiO}_4)\text{O}:\text{Ce}$ ("GSO"). The use of this material as a scintillator is based on a process which converts the energy of high energy particles such as gamma rays into visible light. When gamma rays are absorbed in GSO, many electron-hole pairs are created. Some of these electron hole pairs eventually recombine at the luminescent center, the Ce^{3+} ion, which emits blue light. The gamma-ray excited scintillation decay curve, however, contains a build up and a much slower component than the intrinsic Ce^{3+} decay (22 ns) (Fig. 1). This result suggests that the energy transfer from gamma radiation to Ce^{3+} is relatively slow. One of the possible explanations for this slow transfer process is that energy is transferred resonantly from Gd^{3+} to Ce^{3+} as the emission bands of Gd^{3+} overlap the absorption bands of Ce^{3+} . In order to investigate the energy transfer from Gd^{3+} to Ce^{3+} , the excited $^6\text{I}_7$ (275 nm) and $^6\text{P}_7$ states (313 nm) of the Gd^{3+} absorption bands were excited with pulsed UV light and the luminescent decay from Ce^{3+} was monitored. Fig. 2 shows three decay curves of GSO monitored at the 420 nm Ce^{3+} emission band. The excitation wavelengths of these three curves correspond to the Ce^{3+} absorption band (at 284 nm), the $^6\text{I}_7$ state of Gd^{3+} and the $^6\text{P}_7$ state of Gd^{3+} , respectively. The decay curve excited at 275 nm shows a build up and the decay excited at 313 nm shows a long component, both of which suggest that the observed build up and the slow component with gamma-ray excitation are associated with the energy transfer from the $^6\text{I}_7$ and $^6\text{P}_7$ excited states of Gd^{3+} to Ce^{3+} .

Figure 1

Figure 2

DAΦNE DESORPTION EXPERIMENT

C. L. Foerster and H. J. Halama (NSLS), A. Clozza and C. Vaccarazza (INFN)

DAΦNE main ring uses aluminum chamber and copper absorbers to absorb both the wiggler and dipole radiation with critical energy of 330 and 208 eV respectively. Due to its 5.3 Ampere circulating current and the resulting large photon flux, DAΦNE vacuum system design depends critically on the magnitude of the desorption coefficient. We have, therefore, set up an experiment on the U10B beamline at the VUV Ring of the National Synchrotron Light Source to verify or to update the proposed DAΦNE vacuum system. An aluminum chamber containing a copper absorber at 100 mrad and a beam stop at normal photon incidence are exposed to white synchrotron light beam with a critical energy of 500 eV. Measurements were made of H_2 , CO , CO_2 and CH_4 desorption coefficients as a function of accumulated photon flux, angle of incidence and surface preparation. Based on these data we will predict DAΦNE pressure and conditioning time required for high current operation and design the pumping system that consists of ion and titanium sublimation pumps.

*Work performed under the auspices of the U.S. Department of Energy, under contract DE-AC02-76CH00016.

FIG. A: Photo Desorption.

Results for a copper (DFC) absorber in an aluminum chamber after vacuum bake.

FIG. B: Photo Desorption.

Results for a copper (DFC) absorber in an aluminum chamber after vacuum bake and glow discharge conditioning.

DESORPTION MEASUREMENTS OF COPPER AND COPPER ALLOYS FOR PEP-II C. Foerster, H. Halama and G. Korn (NSLS) and M. Calderon and W. Barletta (LLNL)

PEP-II will be a β meson factory circulating asymmetric beams of 9 GeV and 3.1 GeV having maximum currents of 3.0A. Copper beam chambers and absorbers will intercept resulting synchrotron radiation and it is critical that the dynamic gas load from photo stimulated desorption (PSD) and thermal outgassing is below an eta of 2×10^{-6} molecules per photon. An experiment was set up to measure PSD from 1m long bar samples and a chamber sample, fabricated from selected copper and copper alloys then exposed to white light on beamline U10B. Based on U10B results a prototype chamber was built and will be exposed to white light with higher critical energies of up to 5 KeV, on beamline X-28A at the X-ray Ring of the NSLS. Measurements were made of H_2 , CO, CO_2 and CH_4 desorption coefficients as a function of accumulated photon flux, angle of incidence, sample material, surface condition, and UHV preparation.

*Work performed under the auspices of the U.S. Department of Energy, under contract DE-AC02-76CH00016.

Figure 3. Molecular desorption yields and total gas desorbed for finished Kael Metal C10100 copper after bake (Run 5)

Figure 6. Molecular desorption yields and total gas desorbed for a finished Hitachi C101000 copper chamber after bake (Run 1)

Table 1. Sample bar and beam stop photocurrents in $\mu A/mA$

Run	Material (vendor)	Sample		Beam stop				Diffuse reflection		Surface
		B	GDC	B	B (%)	GDC	GDC (%)	B	GDC	Finish
1,2	C10100 (1)	5.1	—	0.06	1.2	—	—	0.2	—	Machined
3	C15715 (2)	2.9	—	0.05	1.7	—	—	0.01	—	Machined
5	C10100 (3)	7.2	—	0.14	1.9	—	—	0.45	—	Factory
7	C10300 (3)	4.6	—	0.11	2.3	—	—	0.2	—	Factory
9	C10700 (4)	7.8	—	0.55	6.6	—	—	0.4	—	Factory
31	C10100 (3) 25 m	3.6	—	0.08	2.2	—	—	0.006	—	Factory
13	C10100 (1)	4.1	—	0.11	2.6	—	—	0.1	—	Factory
1,2	CHAMBER	8.5	5.3	0.41	4.6	0.34	6.0	0.4	0.1	Factory

PHOTON DESORPTION MEASUREMENTS OF COPPER AND COPPER PLATED BEAM TUBES for the SSCL 20 TeV PROTON COLLIDER*

C.L. Foerster and C. Lanni (NSLS), I. Maslennikov and W. Turner (SSCL)

Relativistic protons circulating in the SSCL 20 TeV Collider emit synchrotron radiation (10^{16} photons/m, $E_{crit} = 284$ eV). This radiation will photodesorb gases from the walls of the beam tube. The 4.2K superconducting magnet bore tubes will act as very long distributed pumps. Build up of cryosorbed gases could severely limit Collider operation and may require a bore tube liner to hide cryosorbed molecules from the photon flux and to increase the H_2 pumping capacity. To predict Collider vacuum performance, photon stimulated desorption (PSD) experiments have been running at the NSLS, BNL and on the VEPP2M storage ring at BINP, Novosibirsk, Russia. At the U10B beamline of the VUV ring at NSLS, beam tube samples were exposed to over 10^{23} photons/m with $E_{crit} = 486$ eV and incident angle = 12 mrad. Unbaked copper and copper plated stainless steel have been tested. In addition, results have been obtained with a 1200G dipole magnetic field and with a 350°C vacuum bake.

*Work performed under the auspices of the U.S. Department of Energy, under contract DE-AC02-76CH00016.

RUN #	MONTH/ YEAR	SAMPLE	NOTE	TOTAL PHOTONS	RFL
1	11/92	Cu Plate/SS	Unbaked	9×10^{22}	0.032 (5%)
2	12/92	Copper	Unbaked	7×10^{22}	0.082
3	1/93	Cu Plate/SS	Unbaked W/B & W/OB	2×10^{23}	0.021
4	3/93	Cu Plate/SS	Unbaked	2×10^{23}	0.110
5	4/93	Cu Plate/SS	Vacuum Baked	7×10^{22}	0.106
6	6/93	#5 Rotated 140°	Vacuum Baked	1.3×10^{23}	0.092
7	7/93	Au Plate/SS	Unbaked	9.6×10^{22}	0.094
8	8/93	Cu Plate/SS	Unbaked	1.09×10^{23}	0.104
9	9/93	Cu Plate/SS	Unbaked	in process	-

TABLE 1: Photo Desorption (PSD) Runs for SSCL.

Copper plated stainless steel were for different vendors and processes for each run. PSD results will be published. Additional runs are planned.

DISSOCIATION ENERGY OF THE BENZENE-WATER VAN DER WAALS COMPLEX

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The intermolecular interaction between benzene and water is a prototype for the ubiquitous hydrocarbon-water systems common in nature. It is also tractable in theoretical approaches to an understanding of the detailed character of the forces. Thus the magnitude of the benzene-water dissociation energy may serve as a benchmark for calibrating theoretical efforts to construct general potential functions for water-hydrocarbon interactions. The method for measuring cluster dissociation energies developed at U-11 was applied to molecular beams containing $C_6H_6 \cdot H_2O$ clusters. The molecular beams were made by expanding 96:3:1 mixtures of He: C_6H_6 : H_2O through a supersonic nozzle. The two critical values are the ionization potential of C_6H_6 and the appearance potential of $C_6H_6^+$ from $C_6H_6 \cdot H_2O$. These were measured to be $IP(C_6H_6) = 9.246$ eV and $AP(C_6H_6^+, C_6H_6 \cdot H_2O) = 9.340$ eV. Figure 1 shows the threshold region for $C_6H_6^+$ from $C_6H_6 \cdot H_2O$. The difference between the above two values is the dissociation energy of $C_6H_6 \cdot H_2O$. We determine $D(C_6H_6 \cdot H_2O) = 0.094 \pm 0.018$ eV $= 2.2 \pm 0.4$ kcal mol⁻¹. This represents the strength of a "hydrogen bond" in the interaction between a water molecule and a hydrophobic partner. Interestingly, it is substantially less than the dissociation energy of the $C_6H_6 \cdot HCl$ dimer, which was earlier determined to be 4.72 kcal mol⁻¹.

Figure 1. Production of $C_6H_6^+$ by dissociative photoionization of $C_6H_6 \cdot H_2O$. The arrow marks $IP(C_6H_6)$.

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THERMOCHEMISTRY OF PERFLUOROETHYLENE/OXYGEN COMPLEXES

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Liquid fluorocarbons display a surprising solubility for oxygen, a phenomenon as yet unexplained. Small animals do not drown when immersed in certain such oxygen-saturated liquids. It has been proposed that emulsions of fluorocarbons with blood plasma be used as a substitute for blood in emergencies, and it was found that with suitable formulations small animals can survive complete blood replacement. To gather fundamental information to better understand fluorocarbon/oxygen systems we are using cluster photoionization to study the prototype system $C_2F_4 + O_2$. The weak complexes $C_2F_4 \cdot O_2$ and $(C_2F_4)_2 \cdot O_2$ were synthesized, along with $(C_2F_4)_2$ and $(C_2F_4)_3$, by free jet expansions of 7.0% C_2F_4 in O_2 , using a room-temperature 0.012-cm nozzle. Analyses of the resulting cluster distributions and the broad-range spectra of several clusters were reported in the 1992 NSLS Annual Report. We have now established, via threshold measurements, important energetic relationships, especially the dissociation energy of the neutral heterodimer $C_2F_4 \cdot O_2$, which is 3.1 ± 0.3 kcal mol⁻¹. This is only a little larger than the value 2.1 ± 0.4 kcal mol⁻¹ that we previously measured for $C_6F_6 \cdot O_2$. The new data are summarized in the Figure. Since the dimeric binding is not exceptionally large, we speculate that the special affinity of fluorocarbons for oxygen may be a colligative phenomenon.

Energy relationships (in eV) in the C_2F_4/O_2 system of mixed van der Waals complexes.

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PHOTOIONIZATION-INDUCED INTRACLUSTER REACTIONS: KINETIC ENERGY RELEASES FOR CHLOROBENZENE/AMMONIA COMPLEXES

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The photoionization of $C_6H_5Cl \cdot NH_3$ to produce $C_6H_5NH_3^+$ has been the subject of several REMPI investigations. The restrictions on this technique left many questions unanswered and features unexplored, however. In particular, there is speculation on the reaction mechanism that assumes that the processes involved are nonstatistical, although there is no evidence that this is so. The kinetic energy analyzer developed at U-11 was used to study this problem. Figure 1 shows the measured kinetic energy release distribution (KERD) of $C_6H_5NH_3^+$ produced from $C_6H_5Cl \cdot NH_3$ at a photon energy of 9.50 eV, 0.56 eV above threshold. The data agree very well with a statistical process, as shown by comparison with the calculated curves (especially the curve for 0.28 eV.) Also, there is no sign of an exit barrier, which would be manifested as a displacement of the maximum to higher energy than predicted by the statistical assumption. Other reaction channels were also studied. The KERD of $C_6H_5NH_2^+$ produced at a photon energy of 17.7 eV, mainly from $C_6H_5Cl(NH_3)_2$, is shown in Figure 2. Even with such a high photon energy, this reaction is also statistical. Here, the energy is 8.9 eV above threshold, so the pertinent statistical curve is for about half that, or 4 eV.

Figure 1. Points, KERD for $C_6H_5NH_3^+$ from $C_6H_5Cl \cdot NH_3$ at 0.56 eV above threshold. Lines, statistical KERDs for energies indicated.

Figure 2. Points, KERD for $C_6H_5NH_2^+$ from $C_6H_5Cl(NH_3)_2$ at 8.9 eV above threshold. Line, statistical KERD at 3.5 eV.

This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

PHOTOIONIZATION-INDUCED INTRACLUSTER REACTIONS: KINETIC ENERGY RELEASES FOR BENZENE/OXYGEN COMPLEXES

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Dissociative photoionization of $(C_6H_6)_2O_2$ to produce $C_6H_6O^+$ occurs only at energies greater than 14.1 eV¹. The onset is therefore 5 eV higher than the thermochemical threshold near 9.2 eV. Seemingly the strong oxygen-oxygen bond (5.1 eV) breaks while the weak van der Waals bond between the benzene ion and the oxygen molecule (0.15 eV¹ in $(C_6H_6 \cdot O_2)^+$) survives. More information was obtained about the dynamics of this reaction through measurements of the kinetic energy release to the product ion, some results of which are shown in Fig. 1, for wavelengths of 750 and 600 Angstroms (photon energies of 16.5 and 20.7 eV.) The mean energies are 54 and 57 meV, respectively, for $C_6H_6O^+$ in the center-of-mass system, near what would be expected for unimolecular decay of excited $(C_6H_6)_2O_2^+$. This conclusion is supported by the approximate "evaporation" shape of the spectra. There is therefore no important participation of nonstatistical processes. The kinetic energy release for $(C_6H_6 \cdot O_2)^+$ (at 700 Angstroms, 17.7 eV) is also shown by a dashed line. This ion is known to be produced exclusively from the neutral dimer¹ $C_6H_6 \cdot O_2$, so its apparent energy distribution comes from the beam temperature of 5-10 K plus the instrumental resolution, mainly the latter.

Figure 1. Distribution of kinetic energy releases in the center-of-mass system for $C_6H_6O^+$ (solid lines) and $(C_6H_6 \cdot O_2)^+$ (dashed line.) The energy scale pertains only to the energy of the ion, not the total energy.

¹J.R. Grover, G. Hagenow and E.A. Walters, J. Chem. Phys. **97**, 628-642 (1992).

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PHOTOIONIZATION OF HYDROXYMETHYL (CD_2OH AND CD_2OD) AND METHOXY (CD_3O) RADICALS : PHOTOION YIELD SPECTRA, IONIZATION ENERGIES AND THERMOCHEMISTRY*

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Photoion yield (PIY) spectra were obtained for CD_2OH , CD_2OD and CD_3O radicals using the discharge-flow photoionization mass spectrometry (PIMS) technique. The radicals were generated via the reaction of F atoms with appropriate methanol precursors. Additionally, CD_3O was produced via the reaction of CD_3 with NO_2 . Ionization energies (IE) were derived from thresholds of PIY spectra: $\text{IE}(\text{CD}_2\text{OH}) = (7.54 \pm 0.02) \text{ eV}$; $\text{IE}(\text{CD}_2\text{OD}) = (7.53 \pm 0.02) \text{ eV}$; and $\text{IE}(\text{CD}_3\text{O}) = (10.74 \pm 0.02) \text{ eV}$ (independent of CD_3O precursor). These results are all in excellent agreement with other recent PIMS and photoelectron spectroscopy (PES) studies. In contrast to the structure in the PIY spectrum reported by Ruscic and Berkowitz (*J. Chem. Phys.* **95** (1991) 4033), supposedly related to vibrational levels in the ion, the structure in Fig. 1 for CD_3O (via $\text{F} + \text{CD}_3\text{OH}$) was removed after correcting for the contribution by an impurity ($m/e = 34$, presumably CD_2HOH , also see Fig. 1) in the CD_3OH sample. The resultant spectrum in Fig. 2 agrees exactly with the one obtained with CD_3O generated via $\text{CD}_3 + \text{NO}_2$. Empirical estimates of $\text{IE}(\text{CH}_2\text{OH})$ and $\text{IE}(\text{CH}_3\text{O})$ were computed that corroborated our assignments.

Figure 1. Upper trace (●), CD_3O photoion yield vs. wavelength, uncorrected, microwave discharge on. $\text{CD}_3\text{OH} + \text{F} \rightarrow \text{CD}_3\text{O} + \text{HF}$. Lower trace (○), methanol impurity, $m/e = 34$, microwave discharge off.

Figure 2. CD_3O photoion yield vs. wavelength by two methods. Upper trace (●): CD_3O from Fig. 1, corrected for methanol impurity. Lower trace (○): $\text{CD}_3 + \text{NO}_2 \rightarrow \text{CD}_3\text{O} + \text{NO}$. Dashed line: threshold at 115.4 nm (10.74 eV).

* This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, D.C., under contract No. DE-AC02-76CH00016.

A DISCHARGE FLOW-PHOTOIONIZATION MASS SPECTROMETRIC STUDY OF THE $\text{BrO}(\text{X}^2\Pi)$ RADICAL: PHOTOIONIZATION SPECTRUM AND IONIZATION ENERGY*

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The photoion yield spectrum of BrO was measured over the wavelength range $\lambda = 106\text{--}122 \text{ nm}$, see Figure 1. Bromine oxide was generated by the reaction of $\text{O}(^1\text{P})$ atoms with molecular bromine. A value of $(10.46 \pm 0.02) \text{ eV}$ was obtained for the adiabatic ionization energy (IE) of BrO from five independent measurements of photoion yield thresholds (corresponding to the $\text{BrO}^+(\text{X}^3\Sigma) \leftarrow \text{BrO}(\text{X}^2\Pi_{3/2})$ transition), see Figure 2. Spectra for both the ^{79}BrO and ^{81}BrO isotopes were very similar and the resultant photoion threshold values were identical, within experimental uncertainty. The only previous determination of $\text{IE}(\text{BrO})$ was derived from a photoelectron spectroscopy (PES) study (Dunlavey *et al.*, *Chem. Phys. Lett.* **53** (1978) 382), from which $\text{IE}(\text{BrO}) = 10.29 \text{ eV}$ was derived. However, the PES study was severely hampered by numerous spectral features that were ascribed to ionization of the following species: $\text{Br}_2(\text{X}^1\Sigma_g^+)$, $\text{O}_2(^1\Delta_g, ^3\Sigma_g^-)$, $\text{O}(^3\text{P}_{2,1,0})$, $\text{Br}^2\text{P}_{1/2,3/2}$ and HBr . Particularly significant interferences due to Br_2^+ and O_2^+ led to a misassignment of both the threshold and the $v(0,1)$ band of the spectrum.

Figure 1. Photoionization spectrum of ^{79}BrO at a nominal resolution of 0.23 nm and 0.2 nm steps between $\lambda = 108.0$ and 122.0 nm . The photoion yield is the ion counts at $m/e = 95$ divided by the light intensity in arbitrary units.

Figure 2. Photoionization threshold region of ^{81}BrO at a nominal resolution of 0.23 nm and 0.1 nm steps between $\lambda = 116.0$ and 121.0 nm . The photoion yield is ion counts at $m/e = 97$ divided by the light intensity in arbitrary units. The onset of ionization is at $\lambda = 118.54 \text{ nm}$ ($\text{IP} = 10.46 \pm 0.02 \text{ eV}$).

* This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, D.C., under contract No. DE-AC02-76CH00016.

A DISCHARGE FLOW-PHOTOIONIZATION MASS SPECTROMETRIC STUDY OF $\text{HOBr}(X^1A')$: PHOTOION YIELD SPECTRUM, IONIZATION ENERGY AND THERMOCHEMISTRY*

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The photoion yield spectrum of HOBr was measured over the wavelength range $\lambda = 108\text{--}121\text{ nm}$. HOBr was generated by the reaction of OH with molecular bromine. The structure observed in the spectrum (see Figure 1) is indicative of an autoionizing electronic state that is excited into a broad Franck-Condon vibrational envelope. Multi-configuration self-consistent-field calculations were employed to ascertain the available states for HOBr^+ . A value of $(10.62 \pm 0.04)\text{ eV}$ was obtained for the adiabatic ionization energy (IE) of HOBr from the photoion threshold (see Figure 2), corresponding to the $\text{HOBr}^+(^2A') \leftarrow \text{HOBr}(^1A')$ transition. A new value for $\Delta_f H_{298}^\circ(\text{HOBr})$ was derived from IE(HOBr) and estimates of $\Delta_f H_{298}^\circ(\text{HOBr}^+)$. The estimates of $\Delta_f H_{298}^\circ(\text{HOBr}^+)$ were derived from $\Delta_f H_{298}^\circ(\text{BrO}) = 30\text{ kcal mol}^{-1}$ and the proton affinity of BrO ($\approx 153\text{ kcal mol}^{-1}$) that was obtained, in turn, by both empirical and theoretical methods. However, the present value (about -2 kcal mol^{-1}) for $\Delta_f H_{298}^\circ(\text{HOBr})$ is too large. This result therefore suggests that the accepted value for $\Delta_f H_{298}^\circ(\text{BrO})$ has been underestimated by at least $6\text{--}7\text{ kcal mol}^{-1}$.

Figure 1. Photoion yield spectrum of HO^{79}Br between $\lambda = 108.0$ and 121.0 nm at a resolution of 0.23 nm and with 0.2 nm steps. The photoion yield is the ion counts at $m/e = 96$ divided by the light intensity in arbitrary units.

Figure 2. Photoionization threshold region of HO^{79}Br between $\lambda = 115.0$ and 120.0 nm at a resolution of 0.23 nm and with 0.1 nm steps. The onset of ionization is at $\lambda = 116.74\text{ nm}$ (IE = $10.62 \pm 0.02\text{ eV}$).

PHOTOIONIZATION STUDIES OF THE BENZENE-ARGON VAN DER WAALS COMPLEX

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Although the benzene-argon van der Waals complex has been used extensively for the study of mode selectivity of the vibrational predissociation process, the dissociation energy is not well established. Various experimental and theoretical estimates tend to center around 150 cm^{-1} or 400 cm^{-1} , i.e. 0.43 or $1.14\text{ kcal mol}^{-1}$. The method for measuring cluster dissociation energies developed at U-11 was applied to this system. The ionization potential of C_6H_6^+ from C_6H_6 in a molecular beam of 0.4% C_6H_6 in Ar and the appearance potential of C_6H_6^+ from $\text{C}_6\text{H}_6\text{-Ar}$ were measured to be 9.246 eV and $9.308 \pm 0.009\text{ eV}$. Figure 1 shows the onset region for C_6H_6^+ from $\text{C}_6\text{H}_6\text{-Ar}$ (the arrow indicates IP(C_6H_6)). The difference between these two values is the dissociation energy of $\text{C}_6\text{H}_6\text{-Ar}$: $D(\text{C}_6\text{H}_6\text{-Ar}) = 0.062 \pm 0.009\text{ eV} = 1.43 \pm 0.21\text{ kcal mol}^{-1} = 500 \pm 73\text{ cm}^{-1}$. This result clearly favors the higher values in the controversy.

Sharp features appear near 11.8 eV in the photoion yield curves of $(\text{C}_6\text{H}_6)_m\text{Ar}_n^+$ cluster ions, e.g. Fig. 2. These are due to intracluster Penning ionization from excitation of the $3p^6 \rightarrow 3p^54s$ argon resonance. The shift of these resonances from the locations in unclustered argon is sensitive to the cluster size. Shifts and signal amplitudes were used to analyze neutral cluster density distributions in the molecular beams.

Fig. 1. Production of C_6H_6^+ by dissociative photoionization of $\text{C}_6\text{H}_6\text{-Ar}$.

Fig. 2. Spectrum of $\text{C}_6\text{H}_6\text{-Ar}$ showing intracluster Penning ionization at 11.77 eV .

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ION-PAIR FORMATION IN THE PHOTODISSOCIATION OF HF AND DF

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We have measured the excitation functions for F^- formation from photodissociation of HF and DF using synchrotron radiation of 0.3 Å bandpass resolution and a supersonic molecular beam apparatus. Both of these functions (see Figs. 1 and 2, respectively) are characterized by an intense, sharp peak (771.6 ± 0.3 Å and 768.6 ± 0.1 Å, respectively) followed by a complex system of weaker peaks extending to shorter wavelengths that is reminiscent of the spectral features found in ion-pair formation in HCl and DCl [Yench et al., J. Chem. Phys., **99**, 4986 (1993)]. It is interesting to note that the energy positions of the initial sharp peaks correspond almost exactly to the thermodynamic thresholds for formation of ion pairs in HF and DF, which may account for the extreme narrowness of these peaks (~ 1 Å FWHM in both cases) in comparison with the weaker peaks that follow to shorter wavelengths. Although the excitation functions for ion-pair formation in HF and DF have been measured before [Berkowitz et al., J. Chem. Phys., **54**, 5165 (1971)], the present higher resolution results should aid in the identification of the Rydberg states responsible for the formation of ion pairs in these systems.

Fig. 1. F^- formation from HF. Fig. 2. F^- formation from DF.POSITIVE AND NEGATIVE ION MASS SPECTROMETRIC STUDY OF SiF_4 A.J. Yench¹, A. Hopkirk², J.R. Grover³, and B.-M. Cheng^{3,4}

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The positive and negative ion yields from photoexcitation of tetrafluorosilane have been measured using synchrotron radiation and employing a supersonic molecular beam apparatus. The positive ions detected in this study over the energy range from ~ 16 to ~ 28 eV were SiF_4^+ and SiF_3^+ , that at an excitation wavelength of 600 Å were found to be present in the ratio of $\sim 1:36$. In Fig. 1 is shown the relative cross section for SiF_3^+ formation recorded with a bandpass resolution of ~ 1 Å that yields an onset (vertical arrow) of 16.17 ± 0.03 eV in good agreement with a previous determination [Creasey et al., J. Chem. Phys., **93**, 3295 (1990)]. Also given in Fig. 1 are the positions of the adiabatic IP's of SiF_4 , from which a more-or-less strong correspondence between the IP values and the SiF_3^+ features can be found.

In Fig. 2 is shown the relative cross section for F^- formation over the energy range ~ 12.4 to 19.0 eV. It displays a well-defined onset (vertical arrow) at 12.98 ± 0.04 eV with extensive structural features following that appear to be associated with ion-pair formation (thermodynamic threshold indicated) involving Rydberg states converging on the SiF_4^+ ground state, whose adiabatic IP value is also indicated in Fig. 2.

Fig. 1. SiF_3^+ formation from SiF_4 . Fig. 2. F^- formation from SiF_4 .

ANGLE-RESOLVED PHOTOEMISSION FROM CuAuI

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We have carried out a series of angle-resolved photoemission measurements from the (100), (001) and (111) faces of CuAuI at room temperature over the photon energy range 20 - 100 eV. Our aim is to elucidate the electronic structure in CuAuI through a combination of photoelectron spectroscopy and first-principles band structure and photocurrent calculations.

At high temperature CuAu has the disordered fcc structure but on cooling it undergoes an ordering transition at about 410 °C, to the CuAuI structure, a one-dimensional, long period superlattice (LPS). On further cooling a second ordered structure, the CuAuI phase, is produced at about 390 °C. CuAuI has the $L1_0$, layered tetragonal, structure with layers of Cu atoms and Au atoms arranged alternately along the [001] direction. There are several motivating factors for studying CuAuI. For example, (i) we hope to be able to understand the driving force for the stabilization of the LPS, and (ii) since the (100) and (001) surfaces have a different (ideal) atomic arrangements we expect their properties to be different.

On the left we show some spectra obtained from the (001) face at normal emission and 12° incidence. The peak in the 2 - 3 eV region is predominantly due to the Cu-related states and those in the 4 - 8 eV range are Au-related. The spectra are strongly photon energy dependent and show also a considerable dependence on the polarization of the incident radiation. We are currently carrying out electronic structure and photocurrent calculations to assist us with the detailed analysis of these data.

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Effect of C Adsorption on the W(100) Surface Studied by Core Level Spectroscopy

P.F. Lyman and D.R. Mullins (Oak Ridge National Laboratory)

While W is one of the most studied substrates in surface science, and C is one of the most common adsorbates, little is known about their interaction. An earlier low energy ion scattering (LEIS) study, however, indicated that despite the succession of LEED superstructures exhibited as a function of C coverage, C atoms always resided in four-fold hollow sites [1]. A study of the adsorption of various C coverages on the W(100) surface was performed using core level spectroscopy (CLS). High resolution photoemission measurements from the W $4f_{7/2}$ core level were made to examine binding energy shifts induced by the C adsorption and/or any attendant surface W rearrangements. Since binding energy shifts are sensitive indicators of local electronic structure, we were able to correlate the relative populations of the shifted W $4f_{7/2}$ components in the present study with prior observations of long-range order (from LEED) and short range structure (from LEIS) to render information about the local electronic environment and structure of the surface C/W layer.

The well-known core level feature associated with the clean W(100) surface is extinguished at submonolayer C coverages, while four additional features (corresponding to surface W atoms bonded to various numbers of C atoms) are introduced upon continued C adsorption (see Fig. 1). We found that the rate of change of the centroid of the W $4f_{7/2}$ peak as a function of adsorbed C changes dramatically near 0.5 ML and again near 0.66 ML C coverages (see Fig. 2). As the change in average C-W coordination per added C atom is constant, the data indicate that a reconstruction in the W layers occurs between these coverages (thereby altering the change in W-W coordination per added C atom). This reconstruction is concomitant with a rearrangement in the C overlayer (as observed by LEED). The behavior of the C-induced spectral features indicates that this reconstruction occurs continuously, while a later structural transition is seen to proceed via nucleation and growth of reconstructed domains.

Research sponsored by US DOE under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

[1] D.R. Mullins and S.H. Overbury, Surface Sci. 193, 455 (1988).

Core Level Spectroscopy Investigation of the bcc Random Alloy $\text{Mo}_{0.75}\text{Re}_{0.25}$

P.F. Lyman and D.M. Zehner (Oak Ridge National Laboratory)

The constituents of a random alloy may preferentially arrange themselves in the surface region so that the surface layers are not stoichiometric (preferential surface segregation). This phenomenon has previously been observed on the $\text{Mo}_{0.75}\text{Re}_{0.25}(100)$ surface using LEED-IV and verified by LEIS. It was found that the outermost atomic layer was occupied predominantly (96%) by Mo atoms, whereas the second atomic layer is enriched (50%) in Re compared to the bulk. Results of our core level spectroscopy (CLS) investigation of the (100) face of this alloy corroborate this behavior, while our measurements of the (110) and (111) faces reveal a strong crystallographic-dependent segregation (see figure). This is only the second report of such a dependence upon crystallographic direction for surface segregation.

Using the surface core level shift (SCS) displayed by atoms in the surface of a transition metal crystal, we probed the relative population of Mo and Re atoms in the surface layer, employing synchrotron radiation to excite the Re $4f$ and Mo $3d$ core levels. For the (100) face, the Re $4f_{7/2}$ core level showed a small component shifted by ≈ 600 meV to smaller binding energy. The small observed surface-to-bulk (S/B) ratio of ≈ 0.15 clearly indicates that the surface stoichiometry is Re-deficient for the (100) face. Emission from the Mo $3d_{5/2}$ core level revealed a Mo SCS of ≈ 500 meV, also to smaller binding energy, with a S/B ratio of ≈ 1.4 . Both the measured Re and Mo S/B ratios are consistent (in a simple exponential attenuation picture, ignoring photoelectron diffraction) with the stoichiometry profile determined by the LEED-IV and LEIS studies.

In contrast to the small Re $4f$ surface feature observed on the (100) face, the (110) face exhibits an intense, well-resolved surface component. The SCS for this face is ≈ 450 meV toward smaller binding energy. The observed S/B ratio of ≈ 1.7 indicates that the surface atomic layer is enriched in Re for this face; the simple exponential attenuation picture suggests the surface layer is $\sim 35\%$ Re. Finally, data from the (111) face do not exhibit a component shifted from the bulk peak by >200 meV, apparently indicating that the surface layer is virtually devoid of Re. H adsorption does not strongly perturb the Re core levels, lending further support to this interpretation.

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Ni ADSORPTION ON W(001) STUDIED BY W $4f$ CORE LEVEL SPECTROSCOPY

S.H. Overbury, D.R. Mullins, P.F. Lyman (Oak Ridge National Laboratory) and N.D. Shinn (Sandia National Laboratories)

Ion scattering studies have indicated that upon annealing sub-monolayers of Ni vapor deposited on W(001) surfaces, a place exchange occurs between surface W and adlayer Ni. To further characterize this surface alloy formation, we have studied the growth of Ni overlayers on W(001) by analysis of the W $4f_{7/2}$ core photoemission spectra. Core level binding energies are sensitive to electronic changes associated with intermetallic alloying. Using photon energies in the range of 70 eV enhances surface sensitivity compared to an x-ray anode source.

W $4f_{7/2}$ core level spectra were obtained as a function of Ni coverage after deposition at 300 K, after annealing to 1000 K to induce surface alloying and after annealing to 1370 K to desorb any excess bulk-like Ni and produce a "surface monolayer." The Ni coverage was monitored by electron induced Auger electron spectroscopy. The coverage was calibrated relative to the maximum coverage obtained at 1370 K, defined as $\theta=1.0$, although the areal density of this alloyed layer is not certain. Core photoemission data (points) and curves (fitted to multiple instrumentally broadened states with Doniach-Sunjić lineshapes) are shown.

As found previously, the clean surface lineshape is a mixture of three states: a bulk state (B), a surface state 360 meV to lower binding energy (S_1) and an unresolved "interface state" (S_2) at intermediate energy 115 meV below the bulk peak. S_1 is attenuated by Ni deposition, more so on the annealed surface (due to alloy formation) than on the unannealed surfaces. A broadening of the envelope implies new state(s) intermediate between B and S_1 present on the 300 K surface resulting from W beneath pseudomorphic Ni. The broadening is reduced upon annealing to 1000 K

yielding a more homogenous surface W environment. By $\theta=1$ (see figure), S_1 is gone, the line is narrowed and is identical for 300 K or 1000 K anneals. It is well fitted by the B state and a second state, I_1 , shifted 120 meV to lower binding energy, comparable in energy but corresponding to a different state than S_2 . This shift is also comparable to the interface state reported for 1 ML Ni/W(110). Above this coverage the intensity ratio of I_1/B depends upon annealing temperature. At 300 K the ratio decreases gradually with coverage to about 70% of the bulk peak. At 1000 K the ratio increases with coverage up to about $\theta=2$ and then decreases (see figure). Intensity changes are accompanied by a shift in binding energy, due to replacement of I_1 by a new state 170 meV below the bulk state, I_2 , evident above $\theta=2.5$. I_2 is attributed to strained layer of W atoms at the interface beneath Ni islands. Above $\theta=2.5$ the ratio of I_2/B is constant with coverage and independent of annealing (below the Ni desorption temperature).

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U13UA

Fragmentations of Alkyl Chlorides following Chlorine L-shell Electron Excitation and Ionization

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(SUNY at Stony Brook), S.L. Hulbert (NSLS BNL)

The fragmentation patterns of a homologous series of chlorinated hydrocarbons; chloromethane, chloroethane, 1-chloropropane, and 2-chloropropane; were studied by selectively exciting a chlorine L-shell electron to the resonances and continuum using monochromatic radiation from the U13UA beamline. The synchrotron radiation was tuned to six photon energies: 1) below the resonance (190eV), 2) 1st resonance, 3) 2nd resonance, 4) above the LIII edge, 5) above the LII edge, and 6) above the LI edge. In all mass spectra, atomic hydrogen is the most abundant ion. Other common masses include CH_n^+ ($n=0,1,2,3$) and Cl^+ . Among these four compounds, only chloromethane produces an appreciable amount of doubly charged chlorine ion. Chloroethane produces a small amount of C^{++} , and both chloropropanes give little or no Cl^{++} . This trend indicates the charge delocalization effect of the carbon chains in the chlorine core hole decay process. The relative intensity of Cl^+ ion to other fragments also reflects this trend in that it decreases with increasing number of carbons. A coincidence map obtained above LI edge of chloromethane shows the major ion pairs are CH_n^+ with Cl^+ , and H^+ with other ions. Doubly charged chlorine is detected with H^+ , but not with any carbon containing ion fragments. Apparently neutral CH_n are produced in this dissociation channel, which does not exist in other alkyl chlorides containing more than one carbon atom. The location of chlorine in the propyl chain also affects the bond breaking position, i.e. 1-chloropropane always produces more CH_nCl^+ than 2-chloropropane. This channel is relatively weak though, as we can see that for all compounds at all excitation energies, the carbon chlorine bond trends to break in the majority of the processes.

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U13UA

Similarities In The Carbonyl Carbon Resonance Auger Decays In Propionaldehyde, Acetone, and Methyl Formate

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Carbon resonances associated with different core hole sites in propionaldehyde and acetone were well resolved (see Figure 1) by using high resolution and high flux monochromatic synchrotron radiation from beamline U13UA. This capability allowed us to obtain the pure decay spectra of selectively excited core hole states.

Resonance Auger decay spectra of propionaldehyde and acetone were measured by beamline U13UA, and methyl formate was done by using the (e, 2e) coincidence technique. The experimental results of these molecules show that the resonance Auger spectra are fingerprints for the atomic site and can be assigned by analogy with model compounds containing only chemically equivalent sites. The carbonyl carbon resonance Auger spectra of propionaldehyde, acetone, and methyl formate, for example (see Fig. 2), are very similar to each other both in peak shapes and positions. Especially, the participator decays at the carbonyl carbon site are almost identical not only in peak positions and shapes, but also in the intensity ratios. It was found in the analysis that after the core electron is excited to the π^* molecular orbital, the electrons relax and re-distribute. The core excited electrons are strongly localized on the carbonyl carbon independent of the surrounding molecular structure, and the spatial distributions are very similar.

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U13UA

FRAGMENTATION OF METHANE AT VARIOUS PHOTON ENERGIES

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S.L. Hulbert (NSLS, BNL)

Time-of-flight mass spectra of methane were obtained with an apparatus described previously¹ at the U13UA beamline at the following photon energies: 285 eV (valence), 287 eV ($1s \leftarrow 3s\alpha_1$), 288 eV ($1s \leftarrow 3pt_2$), 292 eV (K-edge + 2 eV), and 330 eV (continuum). In all five cases, H^+ was the dominant product. Things of interest in these spectra were: (1) C_2^+ was only produced at 285 eV and in the continuum; the relative ion yield in both cases is about the same. (2) The amount of CH_4^+ produced decreases as we move toward higher photon energies and is completely absent at 292 eV. (3) The relative intensity of CH_n^+ fragments for 287, 288, and 292 eV are similar. However the patterns are dramatically different both in the valence and continuum regions.

FIGURE 1: Comparison of mass spectra of methane

1. J. Murakami et al., J. Chem. Phys. 86, 4442 (1987)

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EXTREME ULTRAVIOLET PROJECTION LITHOGRAPHY

R. Freeman, J. Bjorkholm, L. Eichner, L. Fetter, M. Himel, B. LaFontaine, A. MacDowell, Z. Tan, D. Taylor, D. Tennant, W. Waskiewicz, D. White, D. Windt and O. Wood, II (AT&T Bell Labs.), T. Jewell (Opt. Design Consul.), J. Kortright (LBL), K. Nguyen (UC, Berkeley), P. Takacs (BNL), J. Bruning (GCA/Tropel).

The goal of this project is to evaluate the feasibility of extreme ultraviolet (EUV) projection lithography at the sub-tenth micron level. Our most recent progress includes the following:

1. A Ru/B₄C coated Schwarzschild objective¹ has been used to image line and space features from an open stencil transmission mask onto a resist-coated silicon wafer at 6.8 nm wavelength with a resolution better than 0.1 micron (See Figure). In this work we utilized multilayer coatings of Ru/B₄C to provide reflectances of 15% at 6.8 nm; in earlier work we used multilayer coatings of Mo/Si to provide reflectances of 40% at 14 nm. The current resist images are superior to those produced at 14 nm because the resolution is higher and the resist absorption is lower. The lower resist absorption at 6.8 nm results in a more uniform exposure throughout the thickness of the resist and, hence, resist profiles with much steeper sidewalls.

Figure: SEM photo of 0.075 μ m lines and spaces in 60nm thick PMMA. Diagonal line is SEM artifact.

2. The design of a lateral shearing (LS) interferometer for use with undulator radiation at 14 nm wavelength has been completed. In an LS interferometer the interference pattern between an original and displaced (sheared) wavefront gives information on wavefront aberration. Our LS interferometer will be used to determine the image quality of a 10X reduction Mo/Si multilayer-coated Schwarzschild camera to an accuracy of one quarter wave or better at 14 nm. We anticipate that this system, which will be in operation by the end of the year, will ultimately be used for precise alignment of EUV imaging systems.

¹Kortright, J.B., Gullikson, E.M., and Denham, P.E., in Soft-X-Ray Projection Lithography Technical Digest, 1993 (Optical Society of America, Washington, D.C., 1993), pp. 36-37. Supported by AT&T & NIST under Coop. Agreement No. 70NANB1H1115.

Preliminary Soft X-ray Studies of Beta - SiC

M.-L. Shek (NSLS)

We have looked at the (3x2) Si-rich surface phase of beta-SiC(100). Photoemission spectroscopy shows, in addition to the bulk electronic structural features, two surface-derived features of ~ -2.6 eV and ~ -1.6 eV with respect to the Fermi level. The intensities of these features vary as those of surface Si 2p components upward shifted by ~ 0.5 eV to ~ 1.5 eV from the bulk SiC Si 2p core level. These surface-derived valence band features might be related to some surface Si features observed with electron-energy-loss spectroscopy [1]. These and other results will be presented elsewhere [2].

Valence band of beta-SiC (100) showing the existence of two features V1 and V2 for the clean (3x2) surface. (1) (3x2) surface #1; (2) (3x2) surface #2; (3) (3x2) surface #2 after being heated to >1190 K, to induce some surface Si desorption; (4) the suppression of V1 and V2 of (3x2) surface #1 by absorbed oxygen, in an ambient pressure of 4×10^{-11} torr for about 12 hours; (5) surface obtained by exposing a (3x2) surface #3 to atomic H and subsequent heating to ~ 1190 K. The Fermi level is at 60.3 eV in this figure.

[1] V.M. Bermudez, J. Appl. Phys. **66**, 6084 (1989)

[2] to be submitted to J. Vac. Sci. Technol. for the 40th National Symposium of the AVS.

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PHOTOEMISSION STUDY OF $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ QUASICRYSTAL

Zbigniew M. Stadnik and Guowei Zhang (University of Ottawa, Canada)

The discovery of an icosahedral Al-Mn alloy [1] extended the dichotomous division of matter into either crystalline or amorphous solids, by introducing the notion of quasicrystals. This new form of matter has long-range *quasiperiodic* order and long-range orientational order of crystallographically forbidden symmetries. A central problem in solid-state physics is to determine whether this new quasiperiodic structure leads to expected novel physical properties which are found neither in crystalline nor in amorphous materials. In particular, there is considerable current interest in determining the electronic structure of quasicrystals since this is crucial to our understanding of other physical properties. In this work, the valence-band photoemission spectra of the high-quality, single-phase, thermodynamically stable icosahedral $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ have been measured in the photon energy range $h\nu = 35$ to 150 eV.

Valence-band spectra of icosahedral $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$, which were normalized to the photon flux and corrected for the background due to inelastically scattered electrons and for analyzer transmission, measured at various photon energies are shown in Figs. 1 and 2. By taking advantage of the Cooper minimum in the Pd 4d photoelectron cross section at $h\nu \sim 130$ eV, one can see (Fig. 1) that the broad feature at the binding energy $\text{BE} \sim 3.7$ eV below the Fermi level E_F is mainly due to the Pd 4d states. The intensity of the broad feature at $\text{BE} \sim 0.7$ eV changes noticeably near the Mn 3p $\rightarrow$ 3d transition at $h\nu = 47$ eV (Fig. 2), showing that this feature contains a significant contribution from the Mn 3d states. This has been confirmed by the CIS spectra which are not shown here.

The valence-band spectra of icosahedral $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ show no unusual features of width greater than 0.4 eV (the overall resolution) which could be ascribed to its quasiperiodic nature. The low intensity at E_F is indicative of the low $\text{DOS}(E_F)$.

[1] D. Shechtman, I. Blech, D. Gratias, and J.W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).

Fig. 1.

Fig. 2.

This work was supported by the Natural Sciences and Engineering Research Council of Canada.

U-15 Evidence for core-continuum and valence continuum interchannel coupling following core-excitation of N₂

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Following K-shell excitation of N₂, the luminescence yield spectrum shows the same features as the ion yield spectrum shown in Fig. 1. Dispersed luminescence spectra show that the main luminescing species is the N₂⁺ (B²Σ_u⁺) state (valence ionic state) both below and above the N K-threshold and therefore, the luminescence yield which follows the core cross-section, reflects the B²Σ_u⁺ yield. In order to obtain information on the nature of the process producing the singly charged molecular ion both below and above threshold, the yield of the 2σ_u valence photoelectron (removal of which produces the luminescing state) was observed as a function of excitation energy from 380 - 480 eV. The experiment was performed at 54.7° to remove the angular dependence in the photoelectron ejection. The yield of the valence photoelectrons is known to rise sharply at threshold and decrease monotonically at higher excitation energies. Contrary to these expectations, the 2σ_u photoelectron yield follows the luminescence yield above the K-shell threshold for N₂ as shown in Fig. 2. This provides evidence for direct valence ionization following excitation of N₂ above the K-shell threshold, i.e., interchannel coupling mechanism. An estimate of the branching ratios for the three possible processes (X-ray fluorescence, Double excitations followed by resonance Auger decay and interchannel coupling) contributing to the production of the singly charged molecular ion above N K-shell threshold was obtained from the observed photoelectron yield and the luminescence yield. These estimates show that 66 % of the luminescing species result from interchannel coupling, 18 % result from X-ray fluorescence and the remaining 16 % due to double excitation processes.

Fig. 1

Fig. 2

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STUDIES OF TlSr₂CaCu₂O_xF_y HIGH-TC SUPERCONDUCTORS USING FLUORINE K EDGE EXAFS

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Y. Xin (U. of Kansas)

Inclusion of compounds containing fluorine, CaF₂ and SrF₂, in the sintering process to prepare Tl-Sr-Ca-Cu-O 1212 high-T_c superconductors has exhibited dependence of T_c on the total fluorine content (see Table 1). Tracking down the destination of fluorine atoms in the sample appears to be a natural step to understand the observed phenomena. Soft x-ray EXAFS measurements at fluorine K edge have been performed to investigate the local structure about the fluorine atoms in the sintered samples. Similar measurements have also been performed on CaF₂ and SrF₂ as model compounds. The EXAFS(χ) function of the unknowns appears to be very similar to the χ function of the SrF₂ model compound even for samples in which the fluorine atoms came exclusively from CaF₂ (see Fig. 1). This indicates that the majority of F atoms has actually combined with Sr atoms to form SrF₂ phase in all of these sintered samples.

Sample	CaF ₂ / Tl	SrF ₂ / Tl	transition Temp. (K)	zero-resistance Temp. (K)
SX148	0.75	0.00	103	76
SX149	1.00	0.00	103	90
SX150	1.00	0.50	107	102
SX151	1.00	1.00	107	104

Table 1.

Fig. 1. from top to bottom: SrF₂, SX148, SX149, SX150, SX151, and CaF₂

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EVIDENCE FOR RECONSTRUCTION AT STEP EDGES OF W(320)

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N.D. Shinn (Sandia National Laboratory)

Because the chemical and physical properties of a surface depend critically on surface orientation, the study of vicinal surfaces provides a first step away from low-index surfaces towards the understanding of more complicated, highly structured surfaces. Additionally, vicinal surfaces are themselves quite interesting since they provide essentially one-dimensional defects in a two-dimensional environment. Since sites near step edges are often energetically favorable for adsorption, one can envision creating a variety of novel interfaces which take advantage of this one dimensional nature vicinal surfaces. An especially interesting possibility is the creation of one-dimensional magnets by the adsorption of magnetic atoms along the step edges of a non-magnetic substrate. For this purpose vicinal W surfaces may prove ideal since intermixing is minimal for this highly cohesive transition metal.

In order to characterize the electronic and structural properties of a W vicinal surface we have obtained core-level spectra of flat W(110) and the nearby vicinal surface W(320). In this experiment both surfaces have been cut in the same sample. This two-surfaced sample provides not only an absolute reference for the W(320) spectra [via the bulk binding energy from W(110)] but also a reference for surface cleanliness. Matched sets of data obtained at two different wavelengths and scattering geometries for the flat W(110) and stepped W(320) surface are displayed in the figure. Spectra from the (110) surface (solid lines) show two peaks, one from atoms in the second and deeper layers (bulk) and a second at 310 meV smaller binding energy from 1st layer atoms (surface). Because the (320) surface consists of 5-atom-wide (110) terraces (4 terrace atoms and 1 edge atom), the core level spectra from a simple unreconstructed (320) surface are expected to be similar to those from the (110) surface spectra but also include additional spectral weight from the step atoms at lower binding energy due to their even lower coordination than the (110) terrace atoms. As evident in the figure, spectra from the (320) surface (dotted lines) exhibit no such spectral weight at lower binding energy. In fact, between 40 and 60% of the surface spectral weight is closer to the bulk peak than for the flat (110) surface. I.e., only 2 or 3 out of the 5 atoms per terrace have binding energies comparable to W(110) surface atoms.

Given that the edge atoms of the W(320) surface protrude along the (100) direction and that the W(100) surface is prone to reconstruction, a plausible explanation is a reconstruction at the step which shifts both the edge-atom and its nearest-neighbor core-levels to higher binding energy.

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High-Resolution Core-Level Spectroscopy of Metal/W(110) Epitaxy

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Bi-metallic materials used in magnetic superstructures, catalytic chemistry, and high-temperature alloys derive their unique properties from the electronic structure associated with interfacial bonding. However, the two-dimensional order required to measure interface state dispersion and the theory to interpret these data are not always present. We have shown that high-resolution core-level spectroscopy can provide interface-specific bonding information on the atomic scale. This approach is illustrated by measuring W(4f)_{7/2} binding energy shifts for tungsten atoms at epitaxial, (1x1) Fe/W(110), Pt/W(110), and Ni/W(110) interfaces.

Figure 1 illustrates our results for (1x1)Fe/W(110). Upon interface formation, the surface W(4f)_{7/2} peak shifts to lower binding energy, reflecting the direct W-Fe bonding, whereas the bulk peak broadens and shifts to higher binding energy. Careful Doniac-Sunjic lineshape analysis confirms that the latter is due to a new, second-layer tungsten signal, immediately below the interface layer [1]. These are the first experiments ever to resolve individual substrate electronic responses to bi-metallic epitaxy.

Our results, summarized below, show that the chemical bonding at these isostructural interfaces is reflected in subtle, but measurably different, chemical shifts in the first-layer tungsten atoms. Such measurements will be used to test first-principles calculations of interfacial bonding via the equivalent core approximation.

Sample	Atomic layer	ΔE (meV)
W(110)	surface	-320
	bulk	0
Fe/W(110)	interface	-225
Ni/W(110)	interface	-140
Pt/W(110)	interface	+70

Fig. 1: W(4f)_{7/2} spectra, $h\nu=90$ eV, and Doniac-Sunjic lineshape fits for: (a) clean W(110), with bulk and surface components, (b) 1 monolayer Fe/W(110), with bulk, second-layer, and interfacial components

[1] N. D. Shinn, B. Kim, A. B. Andrews, J. L. Erskine, K. J. Kim, and T.-H. Kang, in "Applications of Synchrotron Radiation Techniques to Materials Science," D. L. Perry, N. D. Shinn, R. L. Stockbauer, K. L. D'Amico, and L. J. Terminello, eds. (MRS, Vol. 307, 1993).

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Valence Level Spectral Studies of Crystallinity Changes in Alumina Films as a Function of Pretreatment Temperature.

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Analysis of the valence level O(1s) spectra provides a very effective approach to the evaluation of the development of surface acidity in water-oxidized alumina films as a function of pretreatment temperature. Typical valence band spectra for the room temperature water-grown oxide before and after heat treatment are shown in fig.1a and 1b respectively, where the photoemission intensity is plotted as a function of binding energy (BE). [Note: The BE's are best referenced to the valence band edge and the variations expressed in terms of difference diagrams].

The valence band consists of two broad peaks, the upper valence band is associated with O(2p) states and the lower band with O(2s) states. States in the lower half of each band come from hybridization of Al(2p) and Al(2s) orbitals with the respective oxygen orbitals where the Al-O interaction has a significant covalent character. The feature between 8-10 eV is attributed to hydroxyl species. The trends in the difference spectra for the band of the high temperature treated oxide (up to 450°C) (a) minus that for the untreated oxide (b) is shown in fig.1c. The shift in the loss at 3 eV and the gain at 7 eV is interpreted to result from a stabilization of the Al-O hybridized states which accompanies the change from amorphous to crystalline alumina occurring with temperature. The shift in the loss at 8 eV is interpreted to result from a decrease in hydroxyl content of the oxide.

The results of the valence band binding energy trends can be combined with oxygen 1(s) core level spectral analysis and x-ray absorption spectra to provide a more complete interpretation of both the acid-site behavior and the defect structure of these prototype alumina films as a function of heat treatment.

Figure 1

Interpretation of Ethylene Adsorption on Water-Oxidized Alumina Films using Valence Band Spectral Analysis.

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Valence band spectral analysis can be effectively used to follow detailed changes in chemical bonding with changes in the substrate surface caused, for example, by interaction with an adsorbate such as ethylene on well defined alumina substrates.

Typical valence band spectra studied at -153°C after ethylene adsorption on heat treated alumina oxide films before and after adsorption are shown in fig.1a (before) and 1b (after) together with the difference spectra (1b-1a) in fig.1c for the indicated oxide heat treatment temperatures. In the upper valence band region there are three gain features at 2 eV, 3 eV and 7 eV. All three of these features are attributed to states directly derived from the ethylene adsorption. [A tentative assignment of the orbital features associated with C_2H_5 , $+C_2H_5$, and C_2H_4 adsorbate is also indicated in the difference curve, fig.2c. Space does not permit discussion of these features here]. A loss feature below 2 eV near the top of the valence band, composed primarily of O(2p) nonbonding orbitals are strong participants in the ethylene/alumina bonding. The results on the valence band changes can be correlated with variations in the oxygen core-levels and x-ray absorption spectra, to provide a detailed description of the surface chemistry for these materials. This provides new understanding of the role that surface acidity might play in the formation of reactive carbonium ions.

Significant changes occur in the electronic structure of the alumina films with heat-treatment. New spectral features associated with the ethylene adsorption pass through a maxima for film treatment temperatures between 350-400°C. The most plausible orbital assignment to these features is that of a $+C_2H_5$ molecular ion, the actual charge on which would be moderated by the extent of charge transfer from the alumina surface to the surface complex. Such a species would behave as a C_2 -carbonium ion. All evidence of the C_2H_5 -derived surface species is quenched when the temperature reaches -63°C which indicates that the "carbonium ion" is very reactive.

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Demonstration of X-ray Linear Dichroism Microscopy

X1A

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The polarization dependence of NEXFS can be exploited to image the orientation of specific bonds in (partially) ordered samples via x-ray linear dichroism microscopy. We investigated the structure of thin sections of poly(p-phenylene terephthalamide) (PPTA) fibers (Kevlar) to demonstrate this technique [1]. Three types of Kevlar fibers were investigated: Kevlar 29, 49 and 149, which differ from each other in the degree of crystallinity (Kevlar 149 is the most and Kevlar 29 the least crystalline) and the crystalline orientation along the fiber axis. Butterfly like patterns characteristic of radially symmetric structures have been observed in all three Kevlar fibers when cut at 45°. The contrast of this pattern was reversed as the sample was rotated by 90° about the optical axis. Micrographs of Kevlar 149 are shown in Fig. 1 as an example. Our observations are consistent with the average aromatic ring plane pointing radially outwards.

Fig. 1: Micrographs of 200 nm thick Kevlar 149 fiber section (cut at 45° relative to fiber axis) imaged with the electric field vector in the left-right direction (A) and in the up-down (B) direction at a photon energy of 285.5 eV. This energy selects the aromatic group of the fiber polymer and the butterfly patterns are due to the radial symmetry and orientational order of the fiber. The observed linear dichroism in these images is confirmed by the contrast changes between the two images.

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

Carbon NEXAFS Imaging of PC/PET Blend

X1A

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We illustrate the high degree of chemical specific imaging that can be achieved with the X1-STXM by imaging a polycarbonate/poly(ethylene terephthalate) (70/30 PC/PET) blend. Contrast reversal at high overall contrast is observed between images acquired at 285.36 and 285.69 eV (Fig. 1), a change in energy of less than 350 meV (absolute energy calibration not known to better than 0.3 eV). At these energies, contrast is achieved by exploring subtle differences between absorption resonances associated with the π bonds of the aromatic groups of each polymer. PET has a split peak, due to the proximity of its carbonyl groups to its aromatic groups, whereas PC has only a single peak (its carbonyl groups are separated from the aromatic groups by an ether linkage). The images have been obtained under normal X1-STXM operating conditions, which corresponds to a Raleigh resolution of 55 nm.

Fig. 1: Micrographs of PC/PET blend acquired at a photon energy of 285.36 (A) and 285.69 (B) eV, respectively (see note on energy calibration [1]). High contrast as well as contrast reversal could be achieved with a photon energy change of less than 350 eV.

Characterization of MDI Polyurethane Foam

X1A

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The chemistry of polyurethanes is complex and depends on numerous variables. Segregated phases formed are typically small and not completely isolated from the surrounding matrix. This complexity makes chemical identification of morphological features of phase segregated foams using micro-spectroscopic techniques particularly challenging. We have begun studies of polyurethane foams based on methylene-diphenyl-diisocyanate (MDI), as precipitates are typically large and well segregated from the matrix. The phase morphology of a typical phase segregated MDI-based foam as acquired with the X1-STXM is shown in Fig. 1. It clearly shows the presence of a bimodal distribution of precipitate size. The larger precipitates are about 5 μm in size, while the smaller precipitates are less than 0.5 μm in this particular foam. Since this image was acquired at a photon energy of 285.5 eV, which is strongly absorbed by aromatic groups, the precipitates in the MDI foam have a high aromatic content, while the matrix has a relatively high polyol functionality (aliphatic, R-O-R'). Fig. 2 shows point spectra from the large precipitates and the matrix. The spectra confirm the assessment made from the image that the precipitate has significantly higher aromatic functionality. Comparison of these spectra to those of molecular analogues of the polymer will be utilized in identifying the precise chemical nature of the precipitates and the matrix

Fig. 1: Micrograph of 200 nm thick section of a MDI-based polyurethane foam acquired at a photon energy of 285.5 eV where aromatic groups are highly absorbing.

Fig. 2: Spectra from a big precipitate (solid) and the matrix (dash) of the MDI based polyurethane foam show in Fig. 1.

X1A

SCANNING XANES IMAGING OF MICROHETEROGENEITIES IN COAL

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Scanning transmission X-ray microscopy (STXM) has been used to spatially map aromatic and aliphatic carbon distributions in ultramicrotomed coal thin sections at the submicron level. In addition, microfocus X-ray absorption spectra were recorded at the carbon K edge probing variations in the fundamental chemistry between discrete microscopic and submicroscopic domains within coal. Organic microheterogeneities in coal fall into three compositionally defined classes: exinites, which have high atomic hydrogen to carbon ratios, $\text{H/C} > 2.0$, vitrinites, having $\text{H/C} \sim 1.0$, and inertinites, having $\text{H/C}'s < 0.6$. Such domains are referred to as macerals and are derived from the selective preservation of various plant remains during coalification. STXM analysis of a high-volatile bituminous coal reveals spectacular variation in the carbon chemistry of the individual coal macerals.

For example, the presence of the exinitic maceral cutinite was dramatically revealed through a contrast reversal resulting from cutinite's frequency dependent absorption behavior, i.e. high transmission at a wavelength of 4.34 nm and strong absorption at 4.30 nm (see figure below), corresponding to the relative abundance of sp^2 and sp^3 bound carbon, respectively. This is consistent with cutinite's high H/C ratio inherited from its botanical precursor, waxy leaf cutin. Large regions of the woody tissue derived maceral class vitrinite exhibited significant submicron scale variations in its carbon chemistry, revealing unexpected structural complexity at even the finest scales. Such structural detail may help identify the specific fossil precursors, hence it will benefit paleobotanical analysis. The inertinite macerals include pyrolytic carbon derived from fossilized charcoal; STXM analysis clearly resolved this maceral class allowing for both chemical and microstructural analysis. In addition to chemical and topological information gained, information on bulk density can also be inferred from absorptivity data. Significant variations in bulk density between and within the maceral classes is clearly evident, potentially indicating fundamental differences in each maceral's macromolecular structure. The success of the first application of STXM to the analysis of coal maceral chemistry has clearly been demonstrated.

4.30 nm

4.34 nm

8 μm

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

COHERENT SOFT X-RAY DIFFRACTION FROM NON-PERIODIC OBJECTS

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Following the basic ideas of x-ray structure analysis of single unit-cell specimens by Sayre it should be possible to determine the structure of weakly-scattering non-crystalline material from the radiation scattered from it.^{1,2} The resolution to which the structure can be determined will depend on the maximum scattering angle of the radiation, which, in most biological specimens, will be limited by radiation damage. Even so, imaging relying solely on diffraction should be an extremely powerful x-ray microscopy tool.

A weakly scattering object illuminated by a temporally and spatially coherent beam will give rise to a far-field diffraction pattern that will be equal to the Fourier transform of the object function. This diffraction pattern is a complex wave-field, yet only the intensity of the wave-field is generally measured. Thus, the imaging problem becomes one of providing the phase information to the amplitude of the diffraction pattern, to be able to perform an inverse Fourier transform and arrive at the object data. In the absence of noise, and with the use of *a priori* information about the object, such as its support (the area in which the object is non-zero), it has been shown that the object function can be uniquely determined from the amplitude of its transform.³ Methods used in macromolecular crystallography structure determination can also be employed.

Previous work has shown that it is possible to record diffraction patterns from microscopic non-crystalline objects, using a coherent high-intensity synchrotron x-ray source.^{2,4} In particular, diffraction patterns of individual cells of *Minutocellus polymorphus* have been recorded with 1.8 nm x rays, showing spatial frequencies corresponding to a resolution of 7.0 nm.⁴ This technique has been developed further and has been used to study individual sonicated bull-sperm cells and sperm tails. Experiments have been performed at the short wavelength branch of beam-line X1A. Spatial coherence was provided by a 15 μ m diameter pinhole. The diffraction patterns were recorded on soft x-ray photographic film, at a distance of 25 mm from the sample. In addition to diffraction patterns, we have recorded scanning transmission x-ray microscope and atomic force microscope (AFM) images of samples. Shown in Fig. 1 is the diffraction pattern of a bull-sperm tail, and shown in Fig. 2 is the Fourier transform of an AFM image of a tail.

We have clearly shown that it is possible to record soft x-ray diffraction patterns from microscopic biological objects. As yet we have not attempted to phase a diffraction pattern to reconstruct the object function. We do plan to do this, employing direct detection by a CCD chip.

Fig. 1: Diffraction pattern of a bull-sperm tail, recorded with an x-ray wavelength of 1.8 nm. The black rectangular region is the beam which has scattered from the pinhole and which passes through the silicon nitride window.

Fig. 2: Fourier transform of the height data of an AFM image of a bull-sperm tail. The vertical stripes are artifacts.

1. D. Sayre, *Acta Cryst.*, **5**, 843 (1952).
2. D. Sayre, in *Proceedings of the 1990 Erice School on Direct Methods in Solving Crystal Structures*, ed. H. Schenk, Plenum 1991, p. 353.
3. J. R. Fienup, *J. Opt. Soc. Am. A*, **4**, 118 (1987).
4. D. Sayre *et al.*, in *X-Ray Microscopy II*, Springer Series in Optical Sciences Vol 56 (1988).

X-Ray Gabor Holography

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X-ray holography shows promise as an imaging technique for flash sources. Work at X1A serves to refine the technique in anticipation of the development of suitable flash sources, such as x-ray lasers. Our primary emphasis has been on biological imaging so we use x-rays in the water window (between the O-K and C-K absorption edges). The hologram is recorded on photoresist (PMMA), examined (enlarged), digitized and numerically reconstructed. Previous work¹ demonstrated 56 nm resolution of dried biological specimens. We believe that the TEM used to examine the resists limited achieving higher resolution. Recent work has concentrated on improving this resolution by employing a customized scanning force microscope² to examine and enlarge the hologram. We have completed this SFM and show recent results used to characterize our methodology. The picture is a of a gold wire (diameter = 12 μ m) exposed on PMMA using $\lambda = 1.89$ nm x-rays. The hologram was examined using the SFM and is (512 pixels $\times$ 0.04 μ m)² with the box showing the region that was used to generate the line-plot. This agrees well with the analytical solution for a wire hologram.

¹C. Jacobsen, M. Howells, J. Kirz, and S. Rothman, "X-ray holographic microscopy using photoresists", *J. Opt. Soc. Am. A* **7**, pp. 1847-1861 (1990).

²S. Lindaas, C. Jacobsen, M. Howells, and K. Frank, "Development of a linear scanning force microscope for x-ray Gabor hologram readout", *Proc. SPIE* **1741**, pp. 213-222 (1992).

X1A

X1A

DEMONSTRATION OF HIGH RESOLUTION 3D X-RAY HOLOGRAPHY*

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E.H. Anderson (CXRO/LBL), and D.P. Kern (IBM)

Three-dimensional soft x-ray holography is promising for high resolution study of wet biological objects. X-ray holograms obtained previously¹ show good (60 nm) transverse resolution, but they exhibit little depth resolution due to their limited numerical aperture. Diffraction tomography is an approach to holographic imaging that enables a larger aperture and therefore better depth resolution to be obtained.²

To demonstrate the feasibility of this approach, we recorded Fourier transform holograms of a microfabricated test pattern from various illumination directions (fig. 1), then numerically assembled and reconstructed them according to diffraction tomographic principles. The pattern consisted of two parallel 100-nm wide gold bars, 130 nm thick and spaced 2.5 μm apart. The holograms were recorded with a CCD camera using 3.2-nm x-rays. The incident coherent flux of 5×10^3 ph/ $\mu\text{m}^2/\text{s}$, spatial coherence width of 50 μm and temporal coherence length of 0.5 μm were more than adequate to obtain high contrast fringes with 1-min exposures. 3D reconstructions (fig. 2) of one bar from five holograms covering an angular range of 90 degrees show localization to better than 100 nm in both longitudinal and transverse extent. This work³ indicates that tomographic x-ray holography shows potential for high resolution 3D microscopy.

Fig. 1. Experimental arrangement. Bars are shown in profile; one serves as the reference source, the other serves as the object.

Fig. 2. Four views of a 1- μm segment of object bar, from different orientations. Bar is well resolved in three dimensions.

1. I. McNulty et al., *Science* **256**, 1009 (1992)
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3. I. McNulty et al., *SPIE Proc.* **1741**, 78 (1992)

* Work supported by the U.S. Department of Energy under Advanced Energy Projects Contract W-7405-ENG-48 and BES-Material Sciences Contract W-31-109-ENG-38.

DEVELOPMENT OF BIOLOGICAL APPLICATIONS FOR SOFT X-RAY MICROSCOPY

Mario Moronne, Carolyn Larabell, Paul Selvin, and Robert Glaeser

The following summarizes work by the Lawrence Berkeley Laboratory soft X-ray microscopy team at Beam Line X1A in the past year. There are three main projects that were addressed in relative order of importance:

- a. Development of Fluorescent Probes for Soft X-ray Microscopy
- b. Elemental Mapping of Biological Samples
- c. High Resolution Imaging of Malaria Parasite Infected Human Red Blood Cells

X-ray excited luminescence imaging of biological samples has been made possible by two recent developments: 1) Jacobsen et al (1993)¹ developed instrumentation that allows collection and quantitation of visible light emitted from samples excited by X-ray irradiation using the scanning transmission X-ray microscope (STXM) at beamline X1A, and has detected fluorescence signals from phosphor beads and dye containing latex spheres; 2) Moronne et al (1993)² have further demonstrated that lanthanide based probes are sufficiently radiation hardy to form the basis of a new class of X-ray excitable molecular probes. In August, the LBL group demonstrated the labeling of actin by an avidin-terbium complex at beamline X1A. The latter probe has the potential to be extremely versatile permitting the specific labeling of readily available biotinylated molecules and probes. We believe this work will lead to practical applications of X-ray microscopy to a wealth of biological problems that are currently limited to visible light resolution. It should be noted that this work would not be possible without the dedication and help of the X1A Brookhaven staff.

Progress toward elemental mapping of biological samples has significantly progressed. Initial studies have been made using inorganic potassium salts for calibrations and controls. These results are being used to analyze potassium concentrations in kidney tissue sections provided by Peter Ingram of Duke University. At present, our results have provided valuable information on the constraints applicable to this type of analysis. Software has been developed for correlating multiple images and generating elemental maps. Although quantification of inorganic elements in thin biological specimens represents a serious technical challenge with the presently available X-ray flux at the NSLS, the superior scanning design and spectral purity provided by X1A is crucial to the development of this technology.

In the past year we have initiated high resolution imaging of wet-fixed malaria infected human red blood cells and have obtained some of the best X-ray images of biological samples to date. Parasites have been clearly resolved inside infected cells. The boundaries of the parasitophorous vacuole can be seen as well as dense aggregated material that probably correspond to hemozins (hemoglobin degradation products produced by the parasite). These initial studies will be expanded to include stereo images to detect development of morphological features during the parasite life cycle and fluorescent antibody labeling studies to evaluate the expression of important antigens, particularly those that are thought to be crucial for endothelial adherence.

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2. Moronne, M.M., Larabell, C., Selvin, P., Williams, S. and R. Glaeser (1993). X-ray excitable fluorescent probes for soft X-ray microscopy. *J. of Microscopy*, *in preparation*

Support: This work was funded by DOE grant DE-EC03-76SF00098

FAST X-RAY DETECTORS FOR TIME RESOLVED EXPERIMENTS*

L. Yang and I. McNulty (Advanced Photon Source/ANL)

We have designed and built a fast microchannel plate (MCP) detector assembly with a typical response time of 1 ns. The detector design is similar to those adopted by previous researchers,¹ but it is more compact, UHV compatible, and inexpensive to manufacture. It consists of a single MCP with an anode and shield composed of two concentric aluminum cones with half-angles of 11° and 25° . The coaxial structure provides a close impedance match to 50- Ω cable. The design could easily be adapted to incorporate two MCPs for higher gain. These detectors will be used in a soft x-ray intensity interferometry experiment.² Because the signal-to-noise ratio of an intensity interferometer is proportional to the square root of the electrical bandwidth of the detector system, it is important to use detectors with as fast a response as possible in order to minimize the measurement time.

Timing and linearity tests were performed on the detectors using 400-800 eV undulator radiation at the X1A beamline, with the storage ring operated in single bunch mode. The quantum efficiency¹ is roughly 10% near these energies. We measured output rise times of better than 0.5 ns for both a low resistance gold plated MCP and a standard inconel coated MCP, in the photon-counting (saturated) mode at bias voltages of 900-1000 V, and at count rates exceeding 1.7 MHz (the X-ray Ring pulse rate). This rise time is most likely limited by the bandwidth of our measurement electronics (1 GHz).

We also tested the detectors in current mode operation at bias voltages of 200-900 V. The output current showed good linearity over a dynamic range of 16-23 dB depending on the MCP bias voltage.

Fig. 1. MCP detector assembly. All dimensions are given in cm.

Fig. 2. Output pulse shape from the MCP detector at $\lambda = 2.2$ nm.

1. J. L. Wiza et al., *Nucl. Instr. Meth.* **162**, 587 (1979)

2. E. Gluskin et al., *Nucl. Instr. Meth.* **A319**, 213-218 (1992)

* Work supported by DOE, BES-Material Sciences, Contract No. W-31-109-ENG-38.

CHEMICAL CONTRAST IN BIOLOGICAL IMAGING USING STXM

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The Scanning Transmission X-ray Microscope at X1A has many different contrast mode available besides basic absorption contrast between organic material and water. One such enhanced contrast mechanism is X-ray Absorption Near Edge Structure; in particular, the π^* resonance arising from the double or triple bonds not only signals the bond type and bond concentration, but it also varies with the chemical environment of the atom. As a result, important biological components, such as DNA and protein, give rise to different features at the carbon near edge structure as shown in figure 1.

We are using the carbon XANES signatures to develop an analytic method to separate DNA and protein component distributions in biological imaging. In Figure 1, we show spectra taken from the nucleus and cytoplasm of a Chinese hamster ovarian (CHO) cell, the ratio of C=C peaks for DNA (at 4.275 nm) versus bovine serum albumin (BSA, a protein with a peak at 4.294 nm) is higher in the nucleus than it is in the cytoplasm as would be expected.

Our analysis method involves measuring the cross section of component j at wavelength i to give the linear absorption coefficient μ_{ij} . This is related to the optical density

OD_i via $OD_i = \sum_{j=1}^J \mu_{ij} T_j$, where T_j is the thickness distribution of the j th component. We then

performed a least squares fit to the images to J component distributions within the sample. Figure 2 shows the distribution of DNA, protein and inorganic materials within the cell derived using this method. In figure 2, we confirmed that DNA is mainly concentrated inside the nucleus; and the cell has protein both inside and outside the nucleus; there are also some inorganic materials left due to preparation. Because these distribution of DNA and protein are what would be expected, we have confidence that this approach can be extended to the study of real biological problems.

Fig 1. Spectra of DNA, BSA, and that from nuclei and cytoplasm of CHO cell

Fig 2. Distribution of DNA, protein, and inorganic material derived using multiple wavelength images and the spectra shown in Fig 1.

X1B

Electronic Structure of α - and β -FeSi₂ Studied in Fe L₃ Absorption and Emission

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The electronic structure of ion beam synthesized iron disilicides has been studied, via transitions involving the Fe 2p_{3/2} core excitation. The absorption and emission spectra are compared to predictions based on the unoccupied and the occupied Fe d-density of states, respectively. The agreement is in general good and in particular our results confirm that α -FeSi₂ has Fe d-type states at the Fermi level whereas β -FeSi₂ is semiconducting. We measure the band gap to be 0.6 eV. Correlation satellites in the soft X-ray emission spectra are identified and studied, using monochromatic photon excitation close to threshold.

Using the large penetration length of the photons were also able to follow the process of ion beam synthesis. The spectra from As implanted silicon wafers are compared to spectra from ordered silicide layers created in various annealing procedures. These layers are buried several hundred Angstroms beneath a cap layer, and cannot be reached with electron spectroscopies.

X1B

SOFT X-RAY ABSORPTION SPECTROSCOPY OF MN PROTEINS

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In principle, the high resolution of transition metal L-edges offers a superior way to probe the oxidation states and environment of metalloproteins. Until recently, measurements of Mn metalloproteins were unfeasible due to the high concentration of oxygen in protein samples. The separation between Mn L-fluorescence and O K-fluorescence is only ~ 120 eV and is unresolvable using a 13 element Ge fluorescence detector. Inserting a 4 micron high pass Parylene filter between the sample and the detector resulted in selective attenuation of predominantly oxygen fluorescence. Using this arrangement on X1B, we were able to record the first L-edge spectra of a manganese metalloprotein. We observed both the L_{II} and L_{III} edges of Mn (II/II) catalase, an enzyme responsible for the detoxification of hydrogen peroxide. The protein was a generous gift from the J.E. Penner-Hahn lab (U Michigan), purified by T. Stemmler. The spectra presented below are ~5mM in Mn and have been baseline corrected.

figure 1: The L_{III} edge of Mn(II/II) catalase. Inset shows both the L_{II} and L_{III} edges.

We would like to thank the NIH (GM-44380) for their funding.

NEAR-THRESHOLD BEHAVIOR OF THE SHAKE-UP SATELLITES IN THE C1s PHOTOELECTRON SPECTRUM OF BENZENE

X1B

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The total photoabsorption cross-section of benzene above the C 1s ionization threshold at 290.4 eV is characterized by a narrow intense peak at a photon energy of 293.5 eV and a broad enhancement between 295 eV and 310 eV. In the literature the broad structure is generally discussed in terms of a shape resonance, but there is no agreement as to whether the more intense peak at lower energy is produced by another shape resonance, a double excitation, or a mixture of both. In order to better understand the nature of these structures and their influence on various ionization channels, we have measured partial cross-sections and angular distributions of the C 1s main photoelectron line and the first intense group of shake-up satellites in the photon energy region between threshold and 350 eV. Figure 1 shows two photoelectron spectra of benzene including a band of well-resolved shake-up satellites. Note the different relative satellite intensities, indicating their different dependences on photon energy. Some of the smaller features are only present at low photon energies and are therefore associated with conjugate shake-up processes. We also observe different angular distributions for the individual satellites.

Figure 1: The C1s photoelectron spectrum of benzene measured at photon energies of 300.7 eV and 308.5 eV. The figure shows the original data on a binding energy scale, including a smooth secondary electron background.

This work is supported by the German Minister for Research and Technology.

ELECTRON CORRELATION IN CaF_2 STUDIED IN THRESHOLD EXCITED CORE-TO-CORE SOFT X-RAY FLUORESCENCE

X1B

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In transition metals and compounds with partly filled d-shell one observes a split of the ns-level photoemission lines. This split can be directly related to the exchange interaction between the remaining s-electron and the d-electrons. We propose a new method to study this interaction, with the option to modify the occupancy of the d-level. This can be done in a two-step process, where in the first absorption step a p electron is promoted to the d-level, and in the second fluorescence step an s-electron fills the core hole. We demonstrate the method for CaF_2 which has virtually no d-electrons in the ground state. Following a Ca

$2p^{-1}3d$ excitation a $3s \rightarrow 2p$ core-to-core fluorescence process populates final states of the $3s^{-1}3d$ -configuration. This configuration gives rise to four states, due to the exchange interaction between the 3s electron and the 3d electron, and due to the crystal field interaction. Tuning the energy to structures with known crystal field symmetry, we could unambiguously assign the final states in the soft X-ray emission spectra, and thus the 3s3d interaction energies. We find that the exchange splitting in e_g symmetry, corresponding to orbitals directed in-between the fluorine atoms (0.85 eV) is close to the theoretical value for free Ca^{2+} ions (0.9 eV), whereas the splitting is larger (1.18 eV) for the t_{2g} symmetry. Since the corresponding d-orbitals are directed towards the fluorine atoms, we believe that a anti-bonding interaction results in a local charge concentration for the d-orbitals that increases the s-d overlap and thus the exchange interaction. The data also allows us to draw conclusions about the Coulomb interaction between the core holes and the excited d-electron, as well as the 2p and 3s ionization limits

Fig. 1 Ca core-to-core fluorescence excited at the indicated energies, shown on a "binding energy scale", determined by subtracting the excitation energy from the emission energy. The four vertical lines mark the final $3s^{-1}3d$ final states. At 349.0 eV and 352.3 eV excitation energy the states of t_{2g} symmetry are emphasized, whereas the other excitation energies emphasize e_g symmetry. The states are, in order of increasing binding energy: 3E_g , 1E_g , $^3T_{2g}$, and $^1T_{2g}$.

X1B

Short-lived Paramagnetic States in CaF_2 Populated in Threshold Excited Core-to-Core Fluorescence

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The $\text{Ca}2p^{-1}3s^{-1}$ fluorescence transition in CaF_2 has been measured as a function of excitation energy in the threshold region of the $2p^{-1}3d$ absorption. The exchange splitting of the final $\text{Ca}3s^{-1}3d$ states, reached after populating intermediate atomic-like $2p^{-1}3d$ states, could be determined, together with the differential $3d$ electron screening, comparing a $2p$ and $3s$ hold. It is demonstrated that the $2p_{1/2}^{-1}3d-2p_{3/2}^{-1}$ Coster-Kronig transition is energetically allowed, when the excited state is of t_{2g} symmetry. Additionally, we obtain direct spectroscopic evidence that the $2p^{-1}3d$ states are populated in non-spin-conserving transitions ($\Delta S \neq 0$).

X1B

Antiferromagnetic Coupling at the $\text{Cr}/\text{Fe}(001)$ Interface.

Z. Xu, P.D. Johnson, Physics Dept., BNL, and B. Itchkawitz, Fritz-Haber-Institut, Berlin.

Iron is a ferromagnetic material, chromium with an identical lattice structure is antiferromagnetic. Calculations predict that a single monolayer of chromium on $\text{Fe}(001)$ will be ferromagnetically aligned within the layer but antiferromagnetically aligned to the substrate.[1] The calculations also predict that the chromium will have an enhanced moment of the order of $3.0 \mu_B$, considerably larger than the $0.6 \mu_B$ characterizing bulk chromium. In this study we have used spin polarized core level photoemission to examine the interface between the two materials. The core level is localized and allows us to obtain site specific information.

Comparison of the spin polarization of the Fe and Cr $3p$ core levels clearly shows that the magnetic moments on the two sites are antiferromagnetically aligned. Shown in the figure, the large splitting observed between the minority and majority spin components for the Cr $3p$ level further indicates that the Cr atom does indeed have an enhanced moment. The exact relationship between this splitting and the magnitude of the magnetic moment is however still being examined.

The spin polarization in the Cr core level disappears with the deposition of a second monolayer of Cr. This observation supports the findings of other experimental studies which have indicated that the Cr layers couple antiferromagnetically to each other.[2]

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J. H. Dunsmuir, J. H. Hardenbergh, B.P. Flannery (Exxon)

During this year the evaluation of x-ray microtomography (XMT) as a tool for the characterization of porous media and in particular, oil reservoir rock has been pursued extensively. XMT produces three dimensional x-ray opacity information from 1-5 millimeter sized objects with 1-10 micron resolution. The pore geometry (Figure 1) of reservoir rock obtained using XMT has been imported into geometric and diffusive transport models and used to calculate rock properties such as porosity, permeability and formation factor. Good agreement between these model calculations and laboratory measurements of rock properties has been obtained for rock types with simple structure. The validity of the models for predicting properties of more complex rock types is being evaluated. This work is being carried out as a collaborative effort between Exxon Research & Engineering (ER&E) and Schlumberger-Doll Research (SDR). A concurrent experimental program with Exxon Production Research (EPR) to examine residual saturations and relative permeability using both digital subtraction microtomography (DSMT) and digital subtraction microradiography (DSR) is also underway at X2-B and has obtained initial success.

A preliminary study with David Sarnoff Research Center (DSRC) to evaluate the use of XMT and DSR for the characterization of micromachines has been concluded. If successful, the application of DSRC imaging and parallel computing technology to microtomography data acquisition, processing, analysis and visualization will significantly advance the capabilities of X2-B. In order to study the issues associated with parallel processing on the DSRC "Princeton Engine" a direct Fourier inversion reconstruction algorithm has already been successfully implemented on a parallel processing computer at ER&E.

In a collaborative effort with the Mayo Foundation we have successfully demonstrated the capability of microtomography to measure the structure of the cardio-vascular tree of rodent heart specimens. Whole rodent hearts are scanned using a conventional x-ray source and small core specimens are scanned at high resolution at X2-B (Figure 2). This data will be used in a study of vascular circulation. The Mayo Foundation has sought NIH and NSF funding for a three year research program to continue this work.

Figure 1) 64 cube segment of 512 cube of the pore geometry of Fontainebleau sandstone.

Figure 2) single high resolution CT slice of rat heart tissue.

SUPPRESSION OF STRUCTURAL PHASE TRANSITIONS IN Nd-DOPED $\text{La}_2\text{CuO}_{4+\delta}$

R. Harlow, M. Crawford, E. McCarron and W. Farneth (Du Pont)

In previous studies, we have reported that La_2CuO_4 transforms from one orthorhombic form (LTO, Bmab) to a second orthorhombic form (LTO2, Pccn) when the La has been partially replaced with Nd. The structural difference in these two forms relates to the changes in the tilts of the copper-oxygen octahedra. It has now been determined that the original samples used in the study contained extra oxygen, the amount of which is proportional to the Nd concentration. We have subsequently annealed these samples in N_2 at 450°C for 60 hrs. Iodometric titrations have been used to quantify the amount of oxygen initially present and as a check that the annealing process truly produces stoichiometric compounds. A comparison of the x-ray powder diffraction patterns taken on the stoichiometric materials with those where δ ranges up to 0.030 has clearly demonstrated that small amounts of additional oxygen severely suppress the LTO $\rightarrow$ LTO2 transitions in these materials. Shown below is a plot of the orthorhombicity vs temperature for two Nd compositions. For the sample with Nd = 0.35 and $\delta = 0.030$, the sample gradually transforms over a range of 70° ; for the stoichiometric compound, the transformation is abrupt and, in fact, continues to the point where the orthorhombicity is so small that the sample appears to have mostly converted to the low-temperature tetragonal form (LTT, $P4_2/\text{ncm}$). Extra oxygen appears only to be a factor in the insulating phases of La_2CuO_4 ; when doped with either Sr or Ba, the oxygen content has been determined to be stoichiometric.

The modulation in composite structures $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ from analysis of satellite reflections.

F.K. Larsen and A.F. Jensen (Chemistry Dept., Aarhus University, Denmark), E.M. McCarron (R&D Dept., E.I. du Pont de Nemours & Co., DE) and Y. Gao (SUNY X3 beamline, NSLS).

$(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ is a commonly observed phase in syntheses of ternary and quaternary copper oxides also as a byproduct in syntheses aimed at obtaining the superconducting phase of the Bi-Sr-Ca-Cu oxide. The phase has a composite structure consisting of two interpenetrating orthorhombic lattices, which have identical a and b axis values, but incommensurate c axes. This composite structure is modulated and shows satellite reflections. The two parts of the structure both contain copper atoms linked by oxygen atoms in square planar coordination forming parallel layers. One is a sheet of composition Cu_2O_3 built of connected ladders. The other layer consists of ribbons of composition CuO_2 . Metal atoms are accommodated between the copper-oxygen layers. The same general structure exists in the phase range $(\text{Sr}_{14-x}\text{Ca}_x)\text{Cu}_{24}\text{O}_{41}$, $0 \leq x \leq 8$ but the modulation of the structure changes with the value of x as also evidenced by the change of symmetry in one of the sublattices.

We have previously investigated, using a conventional X-ray tube source, a phase which contains a small amount of Bi besides Sr and Ca (Jensen et al., 1993). Only rather few satellite reflections were included in that analysis because they were hard to measure with the MoK α radiation. Crystals of approximate compositions $x \approx 8$ and $x = 0$ were investigated in the present experiment by measuring (first order, second order) satellite reflections, in total (1109,360) and (1189,541) for $x \approx 8$ and $x = 0$ respectively. 363 ($x \approx 8$) and 307 ($x = 0$) main reflections were measured for scaling purposes. Reflections were measured at the fixed wavelength of 0.6565 Å.

The incommensurately modulated composite structures were analyzed in a four-dimensional formalism using the least-squares program COMPREF (Petricek et al. (1991)). All atoms exhibit significant modulation amplitudes, in particular along the b- and c-axes directions. Atoms in the CuO_2 ribbons have relatively large mean-square amplitudes along the ribbon axis, which support a model of modulated ribbons with some phase disorder of the longitudinal waves. Interatomic distances are calculated considering the effect of modulation.

The analysis revealed that for this composite structure, in fact main reflections contain much information on the modulation. However, including the synchrotron measured satellite reflections in the analysis not only improved the standard deviations of the modulation parameters, but the range of calculated distances also narrowed to intuitively more sensible values as shown for the $x \approx 8$ compound.

	X-ray tube data only	Merge of X-ray tube and synchrotron data
Cu_2O_3 sheets:		
Bonds along $\vec{a}$	1.83(4)-1.94(4) Å	1.874(12)-1.906(18) Å
Bonds along $\vec{c}$	1.64(3)-2.25(3) Å	1.929(12)-1.984(12) Å
CuO_2 ribbons:		
Bonds along $\vec{a}$ and $\vec{c}$	1.77(2)-2.05(2) Å	1.811(16)-1.960(17) Å

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Acta Cryst. A47 (1991) 210-216.

Pd Partial Structure Factor of the AlPdMn Icosahedral Phase

M. de Boissieu (SUNY Stony Brook and LTPCM), P. Stephens (SUNY Stony Brook), M. Boudard (ILL and LTPCM), and C. Janot (ILL)

The atomic structure of the icosahedral AlPdMn phase has been studied by anomalous diffraction at the Pd K edge (24 keV).

A set of 400 reflections were measured at 20 and 1300 eV below the edge, corresponding to $f' = -6.5$ and -2.5 , respectively. The sample was a single grain, ground in a sphere with radius 0.2 mm. In order to extract the Pd partial structure factor, the data sets at the two different energies must be on the same relative scale. The data were appropriately rescaled using a first-order model deduced from previous x-ray and neutron measurements.[1] The thirty strongest reflections were reproduced well by this model, giving confidence in the rescaling of the entire data sets.

Figure 1 shows the Q_{perp} dependence of the partial Pd structure factor, extracted by the difference of the two rescaled data sets. Depending on the parity of the reflection, the structure factors fall in two curves. This confirms that the Pd atoms occupy only two different atomic sites in the six dimensional periodic structure. However, when looking more precisely into the results, a phason Debye-Waller factor must be introduced. This is shown in Fig. 2, where the logarithm of $F_{\text{obs}}/F_{\text{calc}}$ is plotted as a function of $|Q_{\text{perp}}|^2$, the reciprocal vector characteristic of the phason space. A clear trend is observed, which demonstrates the necessity of the consideration of chemical phason disorder. The phason Debye-Waller factor has a value of $B = 1.3$ Å.

Figure 1

Figure 2

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CRYSTALLIZATION KINETICS OF POLY(ϵ -CAPROLACTONE) (PCL)/POLYCARBONATE (PC) BLENDS.

Y.W. Cheung; R.S. Stein, (University of Massachusetts, Department of Polymer Science & Engineering); G.W. Wu; B. Chu (SUNY at Stony Brook, Department of Chemistry)

Evolution of the PCL lamellae in blends of PCL/PC was monitored by synchrotron SAXS. The effects of crystallization temperature, PC concentration and PC crystallinity on the PCL lamellar growth in the PCL rich blends were investigated. Isothermal crystallization was accomplished by rapidly transferring the samples equilibrated at elevated temperature (above the melting of PCL) to the isothermal crystallization temperature by means of a dual-chamber cell.

The lamellar spacing (peak position) for pure PCL remained constant during the course of crystallization as shown in figure 1. The PCL rich blends exhibited scattering even when PCL was completely amorphous. This excess scattering arises from the PC lamellae already present in the blends. Figure 2 shows that the lamellar spacing initially decreased and reached a plateau value. An insertion model, where the PCL crystallized in the mixed amorphous phase between the existing PC lamellae, could easily account for the reduction in the lamellar spacing and the absence of multiple peak. This model is also consistent with the quantitative SAXS studies which suggested random mixing of PC and PCL lamellae in the semi-crystalline/semi-crystalline state.

Figure 1. Synchrotron SAXS for precipitated PCL crystallized at 41 °C

Figure 2. Lamellar spacing and peak intensity for 80PCL/20PC blend crystallized at 41 °C.

A HIGH-TEMPERATURE BONSE-HART ULTRASMALL-ANGLE X-RAY SCATTERING INSTRUMENT

B. Chu, Y. Li, P.J. Harney and F. Yeh (Department of Chemistry, SUNY at Stony Brook)

Conventional small-angle X-ray scattering (SAXS) instruments, such as pinhole collimation, double-mirror focusing collimation, and Kratky block slit collimation, have limited access to the small q range where q is the magnitude of the scattering vector. Generally, a Bragg spacing of ~ 150 nm is the limit using the above SAXS instruments.

In order to study the structures with larger length scales, we constructed a high-temperature ultrasmall-angle X-ray scattering (USAXS) instrument using the double crystal reflection concept proposed first by Bonse and Hart. We used two perfect Ge crystals with channel cuts along the (220) reflection plane. Six reflections were used for each crystal. The instrument was designed in such a way that high-temperature experiments up to $\sim 400^\circ\text{C}$ could be performed.

The instrument was calibrated by using a polystyrene latex suspension in alcohol/water mixed solvent ($v/v=2:1$) with a polymer concentration of 3.2 vol%. The latex, from Dow Chemical, has a claimed nominal diameter of 176 nm. The figure shows the desmeared and structure-factor corrected USAXS profile (diamonds) as well as the laser light scattering (LLS) profile (stars) of the same latex but at a more dilute concentration. A good agreement between LLS and USAXS (in the small q range) was obtained.

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SINGLE CRYSTAL DAFS APPLIED TO THE PHOTOSYSTEM II MODEL COMPOUND μ -DIOXO-(Mn(2,2'-BIPYRIDYL)₂)₂ (BF₄)₃·3H₂O

Y. Gao and P. Coppens (Chemistry Department, SUNY at Buffalo)

The organometallic mixed-valence compound μ -dioxo-(Mn(2,2'-bipyridyl)₂)₂ (BF₄)₃·3H₂O is a model for the oxygen evolving center in Photosystem II, which converts water to dioxygen in green plants. The center is known to contain four manganese atoms which are sequentially oxidized on absorption of photons.

We have recorded the diffraction intensities of a number of reflections as a function of the wavelength across the absorption edge, and as a function of the rotation of the crystal around the scattering vector **H** for the particular reflection. The reflections were selected to have a large contribution from one, and a negligible contribution from the other Mn atom. The pre-edge absorption feature evident in the fluorescence spectrum is especially pronounced in the profile of the Mn(IV) sensitive reflections, and dependent on orientation only for these reflections, indicating that the feature is associated with a transition at this atom. The orientation dependence has been analyzed in terms of a dipolar model for which $I(\psi) \approx \Sigma(e \cdot T)^4$, where **e** and **T** are the polarization vector and the transition moment integral vector respectively, and ψ is the angle of rotation around the scattering vector. Excellent agreement is obtained with two **T** vectors for each molecule, directed along the direction of the bridging Mn-O bonds, as illustrated in the figure for the $\bar{4}44$ reflection.

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THE LOW TEMPERATURE MODULATION IN THE TERNARY CHALCOGENIDE Ta₂NiSe₇

Yan Gao, Albert Spijkerman[†], Auke Meetsma[†], Sander van Smaalen[†] and Philip Coppens (Chemistry Department, SUNY at Buffalo)

The ternary chalcogenide Ta₂NiSe₇ first synthesized by Sunshine and Ibers [1] undergoes a transition to an incommensurately modulated structure near 52.5K. In experiments at about 25K, we have measured both the first and second order satellite reflections. The C-centering present at room temperature disappears on cooling, as is particularly evident from the reflection conditions for the satellite reflections. Though the **q**-vector (= 0.483b*, but variable in the 48–63K range) is compatible with the tentative assignment of the valencies Ta⁴⁺ and Ta⁵⁺ in the trigonal bi-capped and octahedral sites respectively, valence-contrast anomalous scattering studies across the Ta edge show no measurable shift between the two atoms. Though the chemical shift of the edge is less pronounced for tantalum than for lighter atoms, valence differences appear small. The structure of the modulation is presently being analyzed using four-dimensional crystallographic methods.

[†]Laboratory of Chemical Physics, University of Groningen, THE NETHERLANDS

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LAMELLAR STRUCTURE OF A PEO/PPO/PEO COPOLYMER IN XYLENE/WATER MIXTURES

G. Wu, Q. Ying and B. Chu (Department of Chemistry, SUNY at Stony Brook)

Synchrotron SAXS was used to study the structures of Poly(oxyethylene-oxypropylene-oxyethylene) (PEO/PPO/PEO) copolymer (PLURONIC L64) in *o*-xylene and water mixtures. Lamellar structures were observed for L64 in *o*-xylene/water mixtures when the volume fraction of L64 was larger than ~0.4. The lamellar spacing increased with increasing H₂O/EO molar ratio. The effect of xylene on the spacing was much smaller than that of water, especially at low values of H₂O/EO molar ratio. The spacing was almost not affected by temperature over the range of 25°C to 55°C. The Teubner-Strey Model [1] could be used to fit the scattered intensity profiles with low H₂O/EO molar ratio. The correlation length (a reflection of particle size) decreased with increasing temperature and decreasing H₂O/EO value.

Fig. 1. Typical SAXS intensity profile of L64 gel at room temperature. Volume fractions of L64, *o*-xylene, and water are 0.50, 0.25, and 0.25, respectively.

Fig. 2. Lamellar spacing as a function of molar ratio of H₂O/EO. Filled symbols represent the values estimated by using the Bragg equation; Open symbols represent the values deduced by using the Teubner-Strey Model.

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SYNCHROTRON SAXS STUDY OF PHASE SEPARATION OF POLY(*t*-BUTYLSTYRENE)-POLYSTYRENE (PtbS-PS) DIBLOCK COPOLYMER AND PtbS-PS/PS HOMPOLYMER BLENDS

Qicong Ying, Guangwei Wu, and Benjamin Chu (Department of Chemistry, SUNY at Stony Brook) and D.G. Peiffer (Exxon Research and Engineering Company)

Synchrotron SAXS was used to study the influence of solvent on the microdomain formation of Poly(*t*-butylstyrene)-polystyrene (PtbS-PS) diblock copolymer and the transition from microdomain structures to the disordered phase. Fig. 1 shows SAXS profiles of poor solvent mixture (benzene/dimethylformide mixture; Bz/DMF = 80/20 by volume). The temperature effect on a blend of PtbS-PS (PtbS/PS = 50/50 molar ratio) and homopolymer PS (*M* = 4000) was also investigated (as shown in Fig. 2).

The results indicated that poor casting solvent induced microdomain formation of PtbS-PS diblock copolymer. Interdomain distance of sample CB1 (PtbS/PS = 25/75 molar ratio). At room temperature, sample CB2 casted from benzene showed a broad peak, which could be caused by weak chain-segregation during sample preparation. Scattered intensity of the homopolymer-copolymer mixture decreased with increasing quantity of homopolymer PS. An increase in the scattered intensity for the sample containing 52.8 wt% homopolymer, could suggest an inverse microdomain formation.

Fig. 1. Plots of scattered intensities *I*(*q*) (arb. units) vs. scattering wave-vector *q* of PtbS-PS casted from different solvent.

Fig. 2. *I*(*q*) vs. *q* for copolymer blends, CB3+PS (*M*_{ps} = 4000), with different compositions at *T* = 75.66°C.

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X3B1

PHASE TRANSITION IN C_{60} N-PENTANE

G. Faigel, G. Bortel, G. Oszlanyi, S. Pekker, M. Tegze (Research Institute for Solid State Physics, Hungary), P.W. Stephens, D. Liu (SUNY Stony Brook)

At room temperature, C_{60} n-pentane is a typical C_{60} clathrate, with orthorhombic symmetry.[1] The structure may be viewed as alternating stacks of slightly distorted square sheets of C_{60} molecules, with n-pentane molecules in a zig-zag arrangement in the channels between molecules. In order to study the influence of molecular motional disorder on the structure, we have carried out x-ray powder diffraction experiments at low temperature, using 1.15 Å x-rays from Si(111) monochromator and Ge(111) analyzer.

The figures below show the changes in the diffraction pattern from 200 K (upper panel) to 170 K (lower panel). The lattice symmetry changes from orthorhombic to monoclinic, as the angle of the rectangular sheets of fullerenes distort to 91.3° .

We have undertaken to understand these results by performing molecular dynamics simulations. We find flipping motions of the n-pentane at high temperatures, with a coordinated freezing accompanied by lattice distortion as the temperature is lowered.

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X3B1

STRUCTURAL ANALYSIS OF $C_{61}H_2$

P. Heiney, A.N. Lommen, L. Brard, A. Smith, R. Strongin, G. Vaughan (U. of Pennsylvania), P.W. Stephens, D. Liu (SUNY Stony Brook)

We have determined the structure of the annulene, or 6-5 isomer, of $C_{61}H_2$ at both 310 K and 20 K. In this molecule, the 61st carbon bridges a hexagon and a pentagon. At 310 K the structure is fcc with lattice constant 14.1935 Å. The buckyballs are orientationally disordered, presumably dynamically, with the 61st carbon preferentially occupying octahedral voids at a radius of 5.0 Å from the center of the molecule.

At approximately room temperature the structure undergoes a phase transition to simple cubic with a jump in the lattice constant of 0.35%. The diffraction profile at 20 K is shown below. In order to achieve this symmetry lowering, each of the four molecules in the simple cubic cell must become inequivalent. We considered a buckyball in "standard orientation" and rotated it by a certain angle about one of the four $\langle 111 \rangle$ directions, according to the Pa3 space group symmetry. A partial occupation of two angles, 24.8° and 88.8° , produces the best fit to the data. We refined the position of the 61st carbon to two of the 6-5 bonds which point toward an octahedral site.

From the similarity of the phase transitions and ordered structures of this molecule with C_{60} and $C_{60}O$ (in which the oxygen is attached to a 6-6 bond), we conclude that the oxygen and methylene additions do not greatly modify the fullerene-fullerene interaction in the lattice, nor do they seriously obstruct molecular reorientations.

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THE CRYSTAL STRUCTURE OF BaTiO(PO₄)₂

J. A. Kaduk (Amoco Corporation, Naperville, IL) and S. J. Crennell (University of Bath, England)

The crystal structure of the title compound has been solved approximately using the intensity data of Powder Diffraction File entry 36-1467 [1], and refined using laboratory and synchrotron X-ray powder diffraction data.

Bi₂TiP₂O₉ has been known for over 30 years, and is of interest as a phosphor material and for its other optical properties. It has been reported to crystallize in I2/m, but single crystals are invariably twinned. For Z = 2 in I2/m, the Ba, Ti, and P must occupy special positions. The Ba accounts for about half of the scattering power, so the prospects for solving the structure from powder data seemed good. It is difficult to avoid preferred orientation in typical samples, so the structure was solved by Patterson and difference Fourier techniques using the 50 intensities of PDF entry 36-1467 [1].

The structure was refined from experimental patterns of flat plate and capillary samples using GSAS. The dimensions of the body-centered monoclinic unit cell are a = 16.7090(12), b = 5.4481(5), c = 4.7924(3) Å, and β = 94.022(5)°. In I2/m, the Ti occupy centers of symmetry, leading to O-O nonbonded contacts of 1.2 Å along the 2-fold axis. The symmetry was lowered to I2, which resulted in good refinements, and indicated the presence of 5-coordinate Ti. The true symmetry is probably even lower, with the Ba exhibiting pseudo-body centering.

The structure consists of chains of corner-sharing PO₄ tetrahedra and trigonal bipyramidal TiO₅ groups parallel to the a-axis. Four of the Ti-O bonds are 1.96–1.97 Å, while the fifth (one of the equatorial positions) is 1.70(3) Å. The compound is therefore best formulated as Ba₂TiO(PO₄)₂. The Ba are 10-coordinate, and occupy the spaces between the chains. The current refinement can only be considered approximate, since the Ba appear to be related by pseudo-body centering.

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THE CRYSTAL STRUCTURE OF BaYYbF₈

J. A. Kaduk, J. Faber, R. H. Jarman, M. N. Kaminsky (Amoco Corporation, Naperville, IL)

The crystal structure of BaYYbF₈ has been determined from a combined refinement of six data sets: X-ray powder data collected at λ = 1.29366(4) Å on X-7A, powder data collected at λ = 1.12706(6) Å on X3B1, laboratory powder data (CuKα), neutron powder data from the 90° and 148° detector banks of General Purpose Powder Diffractometer (GPPD) at Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory (ANL), and single crystal X-ray data (MoKα). The compound crystallizes in the monoclinic space group C2/m, with a = 6.94534(3), b = 10.47071(5), c = 4.24667(2) Å, and β = 95.5550(3)°; Z = 2.

The Ba is 12-coordinate, and is best described as tetracapped square prismatic. The Ba-F distances range from 2.73–2.91 Å. The Y/Yb site is 8-coordinate, and is best described as square antiprismatic. The M-F distances range from 2.22–2.30 Å. One F is tetrahedral-coordinated, and the remaining two F are planar 3-coordinate.

The Y/Yb sites form a pseudohexagonal network parallel to the ab plane by sharing edges of coordination polyhedra. These layers are joined into a 3-dimensional network by corner sharing parallel to c. The Ba reside in cavities formed by this network.

The average structure has been defined very precisely by this joint refinement, but some questions remain about the local structure. Diffuse features are present in the backgrounds of the X-ray powder patterns. These features can be modeled by a real space pair correlation function with distances of 2.035(7) and 4.209(5) Å. These correspond well to the average Y/Yb-F and metal-metal distances in the crystal structure. Nonrandom occupation of the Y/Yb site may be responsible for these features.

The possibility that these diffuse features arise merely from the overlap of profile tails cannot be ruled out. The peak profiles are "hyperlorentzian", and cannot be modeled exactly using the pseudo-Voigt function available in GSAS. The profiles are broadened anisotropically in an unusual pattern, which cannot be described by a single anisotropic broadening axis. It is possible that the average monoclinic crystals of this material are actually composed of small triclinic domains, and that each domain contains only Y or Yb.

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X3B1

THE CRYSTAL STRUCTURE OF HYDRATED SODIUM ALUMINATE, $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$

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The crystal structure of hydrated sodium aluminate, $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$, has been determined *ab initio* from synchrotron powder diffraction data. The compound crystallizes in the acentric primitive tetragonal space group $P-4_21m$, with $a = 10.53396(4)$ and $c = 5.33635(3)\text{\AA}$, and $Z = 8$. The structure is composed of single layers of corner-sharing AlO_4 tetrahedra, joined into 4- and 8-rings. The topology of the layers is number 18 of Smith and Rinaldi [1]. The layers are bonded together by two types of Na, one 6-coordinate, with nearly ideal octahedral geometry, and the second 7-coordinate, with a capped octahedral geometry. Two independent water molecules also occupy the interlayer regions, forming hydrogen bonds to framework oxygen atoms. One oxygen atom of the Al coordination sphere is a hydroxyl group, which points into the interlayer region.

Viewed approximately down the c-axis (Na = solid circles, water = open circles), the structure is:

[1] J.V. Smith and F. Rinaldi, *Miner. Mag.*, **33**, 202–212 (1962).

The SUNY X3 beamline at NSLS is supported by the Division of Basic Energy Sciences of the US Department of Energy (DEFG0291ER45231). Research carried out in part at the National Synchrotron Light Source at Brookhaven National Laboratory which is supported by the US DOE, Division of Materials Sciences and Division of Chemical Sciences.

X3B1

XAFS STUDIES OF III-V DILUTED MAGNETIC SEMICONDUCTORS

A. Krol, Y. L. Soo, S. Huang, Z. H. Ming, and Y. H. Kao (SUNY at Buffalo) and H. Munekata and L. L. Chang (IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY)

X-ray absorption fine structure (XAFS) measurements were performed at the Mn K-edge on $\text{In}_{1-x}\text{Mn}_x\text{As}$ diluted magnetic semiconductors prepared by molecular beam epitaxy with x ranging from 0.01 to 0.12. It has been found that in the samples prepared at high-growth-temperatures around 280°C , Mn and As atoms form hexagonal clusters with NiAs structure. Only a very small fraction of Mn atoms may substitute for In in the zincblende InAs structure. No significant disorder is observed. In the samples prepared at low-growth-temperatures around 200°C , the majority of Mn atoms form disordered hexagonally coordinated centers with As. The presence of disorder in MnAs centers for the latter case is established using the method of cumulants. Effective valency and coordination of Mn atoms deduced from the near-edge-structure are the same for both the high- and low-growth-temperature InMnAs films. The formal valency is lower than 3, and the average coordination number of the majority of Mn atoms is six. This result of local structure is consistent with the observed difference in magnetic behavior for samples prepared at different substrate temperatures.

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STUDIES OF MICROSCOPIC STRUCTURES OF INTERFACES IN SEMICONDUCTOR HETEROSTRUCTURES AND SUPERLATTICES BY X-RAY SCATTERING AND FLUORESCENCE

Z. H. Ming, A. Krol, Y. L. Soo, and Y. H. Kao (SUNY at Buffalo) and J. S. Park and K. L. Wang (Electrical Engineering Department, University of California at Los Angeles)

The angular dependence of grazing-incidence X-ray scattering and Ge K α fluorescence yield were measured for Si_{1-x}Ge_x/Si and its inverted Si/Si_{1-x}Ge_x heterostructures. The results reveal useful information on the microstructures in these layered materials and show similar interfacial structures in terms of the rms interfacial roughness, correlation-length of height fluctuation, and Ge density profile. Two 10-period superlattices with different layer thickness and Ge concentration were also investigated; correlation between height fluctuations of different interfaces is clearly demonstrated in the data of X-ray diffuse scattering. These results show that X-ray scattering and fluorescence techniques can be employed as convenient tools for nondestructive characterization of epilayer thickness, interfacial roughness, density profile of selected atomic species, and correlations between microstructures of different interfaces in layered materials.

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SUBSTITUTIONAL SITE DISORDER STUDY OF SINGLE LAYER Tl-COMPOUND SUPERCONDUCTOR USING ANOMALOUS SCATTERING

Chan Park and Robert L. Snyder (New York State College of Ceramics at Alfred University)

The chemical occupancies of various cations in high temperature superconductors are directly related to the carrier concentration which determines the superconducting properties. The substitution of an atom by another with different valency changes the hole concentration in the CuO₂ planes. The cation site disorders in Tl-compound superconductors are not fully known. There are a number of reports of structure refinements which have suggested site disorders of Tl on the Ca site, Ca on the Tl site, Cu on the Tl site,[1] and Tl site vacancies. The deficiency of scattering at the Tl site in the Tl-compounds has been well established, but there is no experimental evidence allowing us to attribute it vacant sites, static disorder, or substitution of lighter cations.

The purpose of the present experiment is to investigate the substitutional cation site disorders in the Tl_{0.5}Pb_{0.5}Sr₂Ca₂Cu₃O₇ using the strong variation of the scattering factors in the vicinity of the absorption edges. As the first part of the experiment, synchrotron X-ray powder diffraction data were collected at the lower part of the Cu K edge and well below the edge with intention of determining the possible substitution of Cu on the various cation sites. The temperature factors and atomic positions which were obtained using single crystal X-ray diffraction analysis [2] were used and the occupancies of the cations were refined using the Rietveld least-square method. The theoretically calculated anomalous dispersion terms were used except f' of Cu in the near edge data, which was refined. In this case, the correlation between the f' (Cu) and the occupancy of Cu caused serious problems in refinement. And so, a series of slightly different values of f' (Cu) were used to see if the refinement improved. The result was that no Cu goes onto Sr or Ca sites. The data, however, was not sensitive to the Cu substitution on the Tl site. The presence or absence of Cu on that site gave similar agreement factors. This can be ascribed to the much larger scattering factor of Tl compared to that of Cu, that is, Tl overshadows the effect of Cu. More data will be collected at the Tl L_{III} edge and Sr K edge, and a complete analysis of the cation disorder will be performed.

[1] S. Sasaki et al., *Jap. J. Appl. Phys.* **L467**, (1992).

[2] M.A.Subramanian et al., *Science*, **242** 249, (1988).

The SUNY X3 beamline at NSLS is supported by the Division of Basic Energy Sciences of the U.S. Department of Energy (DEFG0291ER45231). Research carried out in part at the National Synchrotron Light Source at Brookhaven National Laboratory which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences.

X3B1

ORIENTATIONAL PHASE TRANSITION IN Na_xC_{60} ($1 < x < 3$)

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Sodium fullerides are important inasmuch as they do not have superconducting phases, in contrast to the fullerides of potassium and rubidium. We seek an explanation in subtle structural differences in the two materials. [1]

Powder x-ray diffraction reveals an orientational ordering transition in Na_xC_{60} for $1 < x < 3$, similar to that in pure C_{60} , but absent from superconducting K_3C_{60} etc. Specifically, the low temperature phase (see fig.) is simple cubic, Pa3 symmetry, with the same pattern of fullerene orientations as C_{60} . Evidently, the smaller Na^+ ions allow the C_{60} molecules to rotate so as to minimize the orientational part of their intermolecular interaction, whereas K^+ etc. lock them into specific orientations.

Interestingly, the orientational ordering transition occurs at a higher temperature in the sodium fullerides than in pure C_{60} , implying that the Na- C_{60} interaction favors the same ordered state.

X-ray powder diffraction pattern of $\text{Na}_{1.3}\text{C}_{60}$ at 300 K, with Rietveld refinement. The peaks marked with + in the inset are simple cubic, which appear as the sample is cooled below the ordering temperature.

[1] T. Yildirim *et al.*, *Phys. Rev. Lett.* **71** 1383 (1993).

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X3B2

SURFACE X-RAY DIFFRACTION STUDY OF THIN EPITAXIAL FILMS OF C_{60} ON GeS(001)

Götz M. Bendele (University of Hamburg, Germany), Teddy Tse, Peter W. Stephens (SUNY at Stony Brook), Robert L. Johnson (University of Hamburg, Germany)

There have been several recent efforts to grow high-quality epitaxial films of C_{60} on different substrates [1]. It has been shown that such films can be grown on Germanium-Sulfide (GeS), a layered semiconductor with a good one-dimensional lattice match with C_{60} [2].

We conducted a surface X-Ray Diffraction study of thin and monolayer fullerene films between room temperature and $\sim 170\text{K}$. Epitaxial films were prepared in situ by depositing C_{60} from a Knudsen cell to a GeS crystal cleaved perpendicular to its (001) direction and annealing at 475K . Annealing at slightly higher temperatures (510K) gave films of exactly one molecular layer (ML).

Initial diffraction data confirmed that films grow with the $\text{C}_{60}(111)$ axis along the $\text{GeS}(001)$ axis; the $\text{C}_{60}(-101)$ is commensurate by a factor of 0.5 along the $\text{GeS}(010)$ and the $\text{C}_{60}(1-21)$ is incommensurate along the $\text{GeS}(100)$ as proposed earlier [2]. Subsequently we recorded several scans normal to the plane of deposition to determine the structural details of the films (fig.). Analysis of this data is in progress.

In-plane diffraction of the 20ML film showed superlattice reflections at temperatures below 250K in the region of $q > 2.5\text{\AA}^{-1}$, which vanished at higher temperatures. This is strong evidence of the same orientational phase transition that has been reported earlier for the bulk [3]. Further, the thermal expansion of both 20ML and monolayer films was measured to be the same as the substrate's in both commensurate and incommensurate directions. In the incommensurate direction, however, the ratio between the film's and the substrate's unit cell length is different for 20ML and the monolayer, suggesting some residual strain in the film resulting from the $\sim 0.9\%$ lattice mismatch.

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References: [1] e.g. D. Schmicker *et al.*, *Phys. Rev. B* **44**, 10995 (1991)
[2] J.-M. Themlin, G. Gensterblum *et al.*, *Phys. Rev. B* **46**, 15602 (1992)
[3] P. A. Heiney *et al.*, *Phys. Rev. Lett.* **66**, 2911 (1991)

Fig. Q-scan around the $\text{C}_{60}(111)$ peak at room temperature and $\sim 20\text{ML}$ deposition ($\lambda = 1.1369\text{\AA}$; x-axis 2θ)

AN ENERGY DISPERSIVE X-RAY ABSORPTION BEAMLINE

P. L. Lee¹, M. A. Beno¹, G. Jennings¹, M. Ramanathan¹, G. S. Knapp¹, J. Bai², K. Huang¹, and P. A. Montano^{1,2,3} (¹Materials Science Division, Argonne National Lab., ²Brooklyn College of CUNY, ³Univ. of Illinois, Chicago)

An energy dispersive x-ray absorption spectroscopy instrument has been built at the X6A beam port of the X-ray ring. This instrument allows the collection of EXAFS and/or XANES spectra for many elements on the millisecond time scale.

As is shown in the figure, the beamline employs a 4-point crystal bender and a rectangular Si 220 crystal to access incident energies between 6.5 and 21 keV. Because the polychromator focuses the synchrotron beam to a narrow 100 μm line, this experimental apparatus is ideal for XAS experiments in special environments such as at high pressures, for in-situ experiments, and/or for very small samples.

The normalized absorption spectra as a function of energy for a Cu foil sample. The data were collected for times of 5, 50 msec., 0.5 and 5 sec. each spectrum is shifted by 10 eV and 0.3 units along the y axis. For comparison, a spectrum collected one energy point at a time (conventional technique) is also shown.

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INTERMEDIATE- AND EXTENDED-RANGE ORDER IN CESIUM GERMANATE GLASSES

P. Armand (ANL), A. J. G. Ellison, M.-L. Saboungi (ANL), D. L. Price (ANL), M. A. Beno (ANL) and G. S. Knapp (ANL)

The nature of intermediate-range order (IRO) in glasses remains one of the outstanding problems in condensed matter physics. The most general and persistent evidence of IRO is the first sharp diffraction peak (FSDP), the feature observed at low wave vector in the structure factor $S(Q)$ of many systems, including oxide and chalcogenide glasses and complex liquids. The FSDP is characterized by values of the product of its wave vector Q_1 and the nearest-neighbor distance r_1 in the range 2.2-2.8, implying correlation lengths of the order of $2.5 r_1$, greater than the dimensions of the nominal building blocks of the glasses. However, complex glasses, including silicates, germanates, borates and silicates, possess order on a length scale even greater than that of the IRO and characterized by a diffraction peak in $S(Q)$ at lower wave vector than the FSDP. Anomalous x-ray scattering measurements near the Ge K-shell and Rb LIII-shell absorption edges were carried out to determine the nature and origin of this extended-range order in a typical oxide glass, cesium germanate.

The measurements were made with a new diffraction method developed by Beno and Knapp, which employs a curved analyzer crystal and position-sensitive detector to increase the solid angle of the diffracted beam without loss in Q resolution. In addition, the high energy transfer resolution of this method provides direct discrimination against unwanted inelastic processes such as resonant Raman and most of the Compton scattering. These preliminary measurements were promising and indicated the power of the method, while highlighting the need for certain detailed improvements in the application to diffuse anomalous scattering.

An X-ray diffraction pattern for $\nu\text{-(Cs}_2\text{O)}_{0.2}\text{(GeO}_2\text{)}_{0.8}$ is shown in Fig. 1, collected at 200 eV below the Ge absorption edge (11.104 keV).

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Fig.1. Diffraction pattern of $\nu\text{-(Cs}_2\text{O)}_{0.2}\text{(GeO}_2\text{)}_{0.8}$ taken at 200 eV below the Ge K absorption edge.

COMPOSITION STUDY OF Ni/Fe THIN FILM BY USING ANOMALOUS X-RAY REFLECTIVITY

J.M. Bai (Brooklyn College of CUNY), P. A. Montano (Argonne National Laboratory) and M. Tomkiewicz (Brooklyn College of CUNY)

We use anomalous x-ray reflectivity to study the composition profile of a Ni/Fe permalloy thin film. This method allows a more accurate evaluation of the electron density in the film. The effective electron density and linear absorption of the thin film exhibit large changes when the energy of the incident x-ray beam is tuned below, above, close and far away from the respective K-edges of Ni and Fe. We analyze the experimental measurements using the exact theoretical expressions. We obtained the composition profile parameters of the thin film by fitting the five reflectivity measurements. The calculated values of f' and f'' of pure nickel, iron and oxygen are used as known parameters in our fitting.

In our reflectivity calculation, we use linear segments to approach the local electron density profile at interfaces and Gaussian factors to account for rms roughness due to irregularities in the boundary position. We were able to obtain excellent fits to the data and a more accurate profile of the thin film composition.

Fig. 2 Composition depth profile (Gaussian smeared) at the thin film top surface.

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X6B

Fig. 1 Reflectivity data (circle) and model fits (line).

Surface diffraction measured by the "Grazing Incidence - Normal Incidence" technique

M. A. Baysal, M. Shishkov, and J. M. Bloch (Temple U.) and I. Jacob (Ben Gurion U.)

We demonstrated that the normal incidence diffraction can be used to study surface structure. The novelty in this experiment is in that we measured the specularly reflected beam from the surface of a crystal rather than the diffracted beam at the diffraction condition.

The incident x-ray beam is glancing at sub critical angle α on the studied surface of the crystal and at the same time the diffraction angle θ is set to 90 degrees with respect to the surface diffraction. The diffraction condition is attained by tuning the energy of the beam. The diffracted beam is then anti parallel to the incident beam and the two can not be distinguished. At the diffraction condition some of the intensity of the reflected beam is deflected away from the specularly reflected beam into the diffracted beam and a dip in the specularly reflected beam was observed. The shape of this dip has the complementary form to the diffracted beam. This is an inherently surface technique because the measured reflectivity occurs predominantly below the critical angle of the material.

In this Surface Normal Incidence Diffraction (SNID) geometry the inherent width of the diffraction is abnormally wide and therefore materials having lower order would still scatter appreciably.

It should be particularly useful in less ordered materials as compared to the GID technique. In addition to its sensitivity it also yields the phase of the diffraction, information that is not achievable in regular surface diffraction (GID). An unusual feature of this geometry is the surprising increase in the intensity of the reflected beam when the angle of incidence of the of the incoming beam is larger than the critical angle. This phenomenon is a fascinating demonstration of the dynamical nature of this diffraction: In our experiment the diffraction condition occurs simultaneously with surface reflection. Above the critical angle the reflected beam is in opposite phase with the incident beam. Therefore the amplitude of the diffracted beam is subtracted from the amplitude of the specularly reflected beam. This gives rise to an "anti dip" in the specularly reflected beam at the diffraction condition. When the angle of incidence α is varied from below critical to above critical the lineshape of the the specularly reflected beam attains an unusual structure that is the result of the summation of two amplitudes with varying phases.

'Anti-dip' in the specular reflectivity intensity at a subcritical angles of incidence α . (see text)

Observation of X-ray Coherent Scattering at Grazing Incidence

Z. H. Cai, B. Lai, W. B. Yun, I. McNulty, K. G. Huang (Argonne National Laboratory), and T. P. Russell (IBM, Almaden Research Center).

We have observed x-ray speckle at grazing incidence from gold-coated films of symmetric diblock copolymers of polystyrene (PS) and polymethylmethacrylate (PMMA). The polymer films consisted of micrometer-size islands on the surface. A spatially coherent beam was obtained from a monochromatic beam (6 keV) by selecting the coherent photons with a small pinhole, 24 meters from the source. The collimated x-rays were directed at a grazing angle of 0.4 degree onto the sample (10 cm behind the pinhole). The speckle patterns were recorded by a CCD (charge coupled device) detector 115 cm from the sample. The CCD chip has 1024 X 1024 pixels and covers an area of 1.95 X 1.95 cm².

Figures show the scattering patterns recorded with pinholes of different sizes. The patterns obtained using 5 and 12- μ m pinholes clearly show the granular structure familiarly seen in visible light speckle patterns. In the center of each image is the shadow of a beam-stop that prevents the specularly reflected beam from saturating the detector. The two horizontal stripes are due to interference between the scattering from all domain spacings projected onto the axis normal to the x-ray beam. Three line profiles of these scattering patterns along one of the stripes are also shown. As the beam becomes more coherent, the speckle pattern obtained using the 5- μ m pinhole shows higher visibility than those obtained using the 12- μ m and larger pinholes. For the 60- μ m collimating pinhole, the fluctuations are within the photon statistical noise and the speckle is essentially lost. When an annealed film of Au/PS/PMMA without surface domains was used, speckle was not observed, indicating that the speckle pattern arose only from the domain scattering. Speckles due to transverse interferences of islands with length scales up to 150 μ m were clearly identified. X-ray speckle observed at grazing incidence can be used to study inhomogeneous systems where surface and interfacial sensitivity is highly required. This technique may be applied to a large group of non-crystalline materials.

Figures: (above) speckle patterns recorded with a CCD camera from an annealed thin film of diblock copolymers of PS and PMMA. The incident angle was 0.4° and the collimating pinholes were 5 μ m (a), 12 μ m (b), and 60 μ m (c); (right) corresponding line profiles of the speckle patterns along one of the horizontal stripes.

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STRUCTURAL STUDIES OF CHEMICALLY MODIFIED BACTERIAL PHOTOSYNTHETIC REACTION CENTERS (RC) USING EXAFS

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Although crystal structures for a couple of bacterial photosynthetic reaction centers (RC) have been available, following the structural change of the primary electron transfer in RC with time-domain X-ray techniques is not yet done because of the complexity of the system and the limitation of currently available technology. Thus, it becomes desirable to probe the local structural change accompanying the electron transfer reactions in photosynthesis. EXAFS is a simpler technique compared to X-ray diffraction for local structure measurements. However, in the native RC, chlorophylls have Mg, an element which brought up some technical difficulties in EXAFS. A series of EXAFS studies have been conducted on two chemically modified RCs with Ni or Zn on both bridging bacterial chlorophylls (BChl) in the RC (Fig. 1, B_A and B_B). Ni and Zn were chosen to substitute native Mg in the BChl because of their certain similar redox properties and the excited state lifetimes, which are important in electron transfer reactions.

Our first study is focused on the steady-state structure of the modified RC using EXAFS. Compared to the free Ni or Zn BChl (the modified BChl here, one OH group is linked to the BChl_A), the metal to ligand distances and the coordination number of the metal are both changed when the BChls are incorporated into RC protein. The coordination numbers for both Ni and Zn in free BChl are four. The XANES structures of the free Ni BChl suggested a square planar structure because the absorption peak representing 1s to 4p_z transition is very distinct in the XANES region. The coordination number for the metal increases from 4 to 5 or 6 in the modified RC at 20K. Thus, the absorption peak in the near edge for modified RC is much less distinct (Fig. 1), which implies distortion from the square planar structure and agrees with the observed coordination number change. In addition, the Ni-N distances in free Ni BChl are shorter than that in the RC protein (Fig. 2). This is expected as Ni stays out of the macrocycle plane and the nearby histidine from the protein is coordinated with Ni. The Zn-N distances, on the other hand, are slightly shorter in the protein compared to those in the free BChl. For both Ni and Zn modified RC, the coordination numbers are around 4 at room temperature, but are close to 5 or 6 at 20K. This may imply a structural change as a function of temperature around B_A and B_B in the RC. A systematic data analysis of the results is in progress. The above statements should be considered preliminary.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract W-31-109-Eng-38.

Figure 1. XANES of modified RC and BChl_A at 20K.

Figure 2. Fourier back transform spectra of the first shell for modified RC and BChl_A at 20K.

X6B

GERMANIUM NANOCLUSTERS

CHEMICAL VAPOUR DEPOSITION OF DIGERMANE IN ZEOLITE Y AND MORDENITE

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The chemical vapor deposition (CVD) of digermane (Ge_2H_6) within the diamond lattice of $13\text{\AA}$ supercages of zeolite Y as well as in the unidimensional $6.5\text{\AA} \times 7.0\text{\AA}$ elliptical main channels of mordenite, has been employed to assemble intrazeolite germanium nanoclusters. In this process, Ge_2H_6 molecules are anchored to Brønsted acid sites in the α -cage of dehydrated zeolite HY and the main channel of dehydrated HNaM. Saturation loadings, respectively, correspond to 32 Ge_2H_6 per unit cell of HY and 4 Ge_2H_6 per unit cell of HNaM. Mild, vacuum thermal treatments of these samples, induce a series of H_2 elimination and aggregation reactions to yield germanium nanoclusters. The picture that emerges from PXRD, FTIR, MS, SEM-EDX, EXAFS, XANES, XPS and optical reflectance data, is that of intrazeolite hydrogen-bonded $\text{Z-OH} \cdots \text{H}_2\text{GeGeH}_3$ precursors that at about 200°C self-assemble topotactically to produce $(\text{Ge}_8)_8\text{-Y}$ and $\text{Ge}_8\text{-NaM}$ octagermacubane-type nanocluster lattices.

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X6B

DIFFRACTION OF Co/X MULTILAYERS USING ANOMALOUS DISPERSION ENHANCEMENT

C. L. Foiles, R. Loloe and M. Franklin; Physics Department and MSU-Center for Fundamental Materials Research, Michigan State University

Structural transformations of Co in Co/X multilayers appear to be numerous and important factors in the magnetic behavior of these systems. However, there are serious conflicts in results reported in the literature. The Co/Mo system provides a striking illustration of effects and conflicts. Sato [1] reports HCP and BCC structures for Co and attributes the loss of magnetism as the Co layer thickness decreases to magnetically "dead layers". Wang, et al. [2] report only FCC and HCP structures for Co in Mo/Co. They find larger saturation magnetizations than Sato for comparably thick Co layers and attribute the loss of magnetism for thin Co layers to the formation of intermetallics at the Co/Mo interface. All structural results are based upon observation of a very limited number of lines.

We are just beginning some systematic structural studies of Co/X multilayers. Transmission electron diffraction (TED), EXAFS and anomalous dispersion enhancement of X-ray diffraction (AXRD) studies are planned. Initial TED results provide numerous Bragg lines but thus far nearly all the lines are associated with the X component. Only TED data for Co/Cu has produced lines that might be associated with Co. Moreover, the one strong TED line that can be associated with Co raises an interesting question since it matches an expected HCP line which normally has zero XRD intensity in pure HCP Co. Galtier, et al. [3] have observed the same line using TED. To gain further insight into this situation we have attempted to use anomalous dispersion to alter the intensities of Co lines in XRD data. Our initial AXRD results are recent, Aug. 1993, and thus the time for analysis has been very limited. Nevertheless, we can report the following results. One, no single line associated with Co has been observed with the exception of samples where the layer thicknesses are so large that separate Co and X lines appear rather than an average Bragg line for the bilayer unit. Two, systematic variations in satellite intensities occur for Co/Cu when an average Bragg line is formed. More careful analysis of relative intensity patterns and comparison of these patterns to those predicted from models are needed before any significance can be associated with these systematic variations.

These data were taken on line X6B at NSLS and the help of Peter Lee is gratefully acknowledged. We also gratefully acknowledge support for the MSU-CFMR and The Research Corporation.

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Diffuse Scattering from Epitaxial CoSi₂ Columns Embedded in Si(111)

K. G. Huang (MSD, ANL[†]), and R. W. Fathauer (JPL, Caltech)

Epitaxial growth of CoSi₂ on Si has been actively studied for several years, and high quality films have been grown on Si and overgrown with epitaxial Si. Recently, a new technique has been developed to grow columns of single-crystal CoSi₂ surrounded by epitaxial Si on Si(111) surfaces. This phenomenon of columnar growth depends on the growth conditions: the column diameter and spacing may be controlled independently via the Si:Co ratio of co-deposition and the growth temperature, respectively. The knowledge of structure and dynamics is important to the understand of the growth mechanisms.

X-ray scattering studies of thin films and their interfaces can provide detailed information on atomic structures as well as the interfacial morphology. For a two dimensional system, high resolution measurements of diffuse scattering out of the specular scattering plane, at a grazing incidence geometry, yields a stronger signal and simpler scattering pattern. A number of systems have been investigated using this technique. As an example, the results of a diffuse scattering measurement of a sample with columnar CoSi₂ embedded in Si(111) is described below. The 1000Å film sample was grown at 700°C with Si:Co ratio of 12:1 which produces columns of 70 nm and 110 nm approximately in diameter and spacing, as observed from planar TEM micrographs.

The Q_y scan shown in the figure was taken (normal to the scattering plane: $Q_x Q_z$) at glancing angle $\theta = 0.3^\circ$, using a triple bound Ge(111) analyzer in front of the detector. A strong and highly structured scattering was observed on both sides of the sharp specular reflection. A preliminary data analysis shows that the scattering function can be described by a model consisting of one Gaussian central peak and four Lorentzian peaks. The solid line is a fit to the data. The measured scattering contains relatively sharp diffuse peaks at $\pm 1.43 \times 10^{-3} \text{ \AA}^{-1}$ and broad peaks at $\pm 6.63 \times 10^{-3} \text{ \AA}^{-1}$ corresponding to peaks in the distribution function of column spacings in real space at 440nm and 100nm, respectively. The fact that the peaks closer to the center are sharper than other ones suggests that the CoSi₂ columns have a long range correlation. A detailed analysis is in progress to obtain complete correlation functions of the CoSi₂ columns.

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THE ANL X6B BEAMLINE AT NSLS: A VERSATILE FACILITY

K.G. Huang, M. Ramanathan, and P.A. Montano (MSD, ANL[†])

The X6B beamline has recently been upgraded by installation of a double focusing mirror. At present, the main components of the X6B beamline include premonochromator slits, a double crystal fixed-exit Si(111) monochromator, a double focusing x-ray mirror, and a 6 circle HUBER diffractometer. With the high intensity, high energy resolution, and tunability available, the X6B beamline has become a versatile facility for a variety of experiments.

The cylindrical rhodium coated fused silica mirror is located 12 meters from the source (1:1 focusing) and is bent to focus the x-ray beam both vertically and horizontally. The inset of the figure shows the intensity profile of the focal point, of which the FWHM is about 0.65 mm. The incident angle of the beam to the mirror (θ) can be adjusted to obtain high energy photons with higher beam intensity. The x-ray intensities as a function of beam energy measured in different configurations were showed in the figure. At 1:1 focusing, a total flux of 3×10^{11} photons/sec was obtained at 8 keV and 100mA electron current.

The beamline can be operated in either focused beam or unfocused beam modes depending on the experimental requirements. With focused beam, many experiments have been carried out such as x-ray reflectivity and diffuse scattering, surface diffraction, powder diffraction, energy dispersive diffraction, diffraction anomalous fine structure (DAFS) and XAFS, while the unfocused beam have been used for coherent scattering and dynamical diffraction experiments. The X6B PRT members and general users have made significant contributions to X6B scientific programs on materials science research, as described in the experiment abstracts.

† Work supported by US DOE, BES-MS, under contract W-31-109-ENG-38.

DEVELOPMENT OF A NEW SMALL ANGLE SCATTERING TECHNIQUE

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Currently there are two widely used methods for SAXS. One method uses an area detector to take the whole diffraction pattern at one time. This method is very fast, but it can suffer from high backgrounds, particularly if there are elements in the sample which fluoresce. The other method uses a multichannel monochromator after the sample which almost completely eliminates background but allows only one angle at a time to be measured. Using a variation of a powder diffraction technique which we recently developed, we have begun to test a method which may possess the advantages of both SAXS techniques. As shown below, this method uses a focusing exit beam monochromator and a linear position sensitive detector. Fluorescence, slit scattering and scatter from windows and air in the vicinity of the sample can be almost eliminated. This new method allows a range of angles to be measured at the same time thereby increasing the count rate by a large factor.

The results of the first trials of this technique are shown below which displays the SAXS pattern of collagen fibers taken in one minute using the new technique. The most prominent peaks in the pattern are the sixth, ninth and twelfth order diffraction peaks from the 650 Å fibers.

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X6B

NEW TECHNIQUES FOR SYNCHROTRON POWDER DIFFRACTION STUDIES

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We have tested two new powder diffraction methods on the X6B beamline. Both methods utilize analyzer crystals in combination with position sensitive detectors to achieve high resolution, low background and very high counting rates. The first method uses a curved perfect crystal analyzer diffracting in the scattering plane to diffract a range of angles into the position sensitive detector. The second method is somewhat simpler, it uses a graphite analyzer crystal diffracting out of the scattering plane.

Data taken on a Al_2O_3 plate using both methods is shown above. The left figure shows data taken with the focusing crystal method. The resolution (approximately independent of angle) was less than 0.03° . Data for the same sample taken using the out of plane method is displayed on in the right figure. For this method the resolution is angle dependent and varies from 0.03° at low angles to about 0.1° at 100° .

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X6B

Copper K-edge and Sulfur K-edge Glancing Angle XAFS on the Tarnish Film Formed on Copper during Oxidation and Sulfidation

I. Song, B.I. Rickett, P. Janavicius, J.H. Payer, and M.R. Antonio (Case Western Reserve University)

As a part of a research program to identify the process and the products of the oxidation/sulfidation of copper during the exposure to a humid environment containing SO_2 as a pollutant gas, experiments were conducted at two absorption edges: 1) copper K-edge glancing angle XANES (2500 Å copper on float glass substrate), and 2) sulfur K-edge XANES of various sulfur-containing compounds that may model the resulting tarnish product between copper, SO_2 , O_2 and H_2O . The glancing angle copper K-edge XANES data in Figure 1 show some difference in chemical states between the surface and the bulk of copper. The data analysis with anomalous absorption correction on glancing angle data is in progress. In Figure 2, the total electron yield (TEY) sulfur K-edge XANES of various model sulfur compounds are shown. The XANES of those sulfur compounds differ greatly. Very well-resolved primary absorption peaks of sulfide (1s-a, 2469.2 eV), sulfate (1s-t, 2479.9 eV), sulfite (1s-e, 2475.5 eV), bisulfite (1s-e, 2473 eV) species are apparent. Thus, the present experimental energy resolution appears to be sufficient (ca. 0.7 eV max.) to resolve primary absorption features of the sulfur species, and therefore the sulfur K-edge XANES technique seems to be an appropriate choice for identifying the species formed during the oxidation/sulfidation of copper. The TEY data were collected simultaneously with fluorescence data, and the comparison of the two types of XANES data suggests (shown in Figure 3) that the surface of sulfide (CuS) exposed to air is heavily contaminated with sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) probably because of the reaction of CuS with moisture and oxygen. Note that the sulfate contamination is noticed as a small hump (ca. 2480 eV) in the TEY data even in CuS (ultra dry) which was kept dry. This indicates the extreme difficulty of maintaining a sulfate-free sulfide and further implies the absolute necessity of carrying out an *in situ* SO_2 exposure experiment for the identification of the sulfur species formed at the initial stage of oxidation/sulfidation.

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X7A THE WATER STRUCTURE IN THE ALUMINOPHOSPHATE MOLECULAR SIEVE VPI-5 AT 80°C

Javier de Oñate, Christian Baerlocher and Lynne McCusker (ETH, Zurich, Switzerland)

At room temperature, the as synthesized form of the aluminophosphate molecular sieve VPI-5 has a triple helix of H-bonded water molecules following the 6_3 -axis down the 18-ring channels.¹ When a sample is heated to 80°C in a sealed container, two of the three peaks in the ^{31}P MAS NMR spectrum coalesce.² This is indicative of a symmetry change from $P6_3$ to $P6_3cm$, and of the destruction of the ordered water structure. To investigate this transformation structurally and to verify the symmetry change, a sample was sealed in a 1mm quartz capillary, placed in a furnace on the powder diffractometer on beamline X7A, and heated to 80°C. Once the temperature had equilibrated, high resolution powder diffraction data ($\lambda = 0.6998 \text{ Å}$) were collected. Preliminary refinement results indicate that the symmetry is still distinctly $P6_3$ and not $P6_3cm$ as expected. Location of the water molecules is in progress.

Preliminary observed (top), calculated (middle) and difference (bottom) profiles for the Rietveld refinement of VPI-5 at 80°C. To show more detail, the first peak has been cut at 1/5 and the second part of the pattern rescaled.

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EXTENDED RANGE ORDER IN GLASSES

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The nature of intermediate-range order (IRO) in glasses remains one of the outstanding problems in condensed matter physics. The most general and persistent evidence of IRO is the first sharp diffraction peak (FSDP), the feature observed at low wave vector in the structure factor $S(Q)$ of many systems, including oxide and chalcogenide glasses and complex liquids. The FSDP is characterized by values of the product of its wave vector Q_1 and the nearest-neighbor distance r_1 in the range 2.2-2.8, implying correlation lengths of the order of $2.5 r_1$, greater than the dimensions of the nominal building blocks of the glasses. However, complex glasses, including silicates, germanates, borates and silicates, possess order on a length scale even greater than that of the IRO and characterized by a diffraction peak in $S(Q)$ at lower wave vector than the FSDP. Anomalous x-ray scattering measurements near the Ge and Rb K-shell absorption edges were carried out to determine the nature and origin of this extended-range order in a typical oxide glass, rubidium germanate.

X-ray diffraction patterns for $\nu - (\text{Rb}_2\text{O})_{0.2}(\text{GeO}_2)_{0.8}$ are shown in Fig. 1, collected at (a) 13 and 200 eV below the Ge absorption edge (11.104 keV), and (b) 19 and 300 eV below the Rb absorption edge (15.202 keV). The intensity of the EROP is seen to be positively correlated with the scattering amplitude of Ge, but *negatively* correlated with that of Rb. This behavior can be explained in terms of chemical ordering involving metal atoms if S_{RbGe} is negative and S_{RbRb} and S_{GeGe} are positive at the wave-vector corresponding to the EROP. In addition, the large size of the Rb ions must cause a deficiency of oxygen nearby, leading to oxygen-oxygen correlations and enhancing the magnitude of the EROP in the neutron diffraction patterns. The FSDP, on the other hand, has a positive derivative with respect to changes in the scattering amplitudes of both Rb and Ge, indicating that Rb-Ge and Ge-Ge, and perhaps also Rb-Rb correlations, are contributing positively to this peak.

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Fig.1. Diffraction patterns of $\nu - (\text{Rb}_2\text{O})_{0.2}(\text{GeO}_2)_{0.8}$: (a) at 200 eV (closed symbols) and 13 eV (open symbols) below the Ge K absorption edge; (b) at 300 eV (closed symbols) and 19 eV (open symbols) below the Rb K edge.

DIFFRACTION OF Fe/Cr USING ANOMALOUS DISPERSION ENHANCEMENT

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Fe/Cr multilayers formed by alternating Fe and Cr layers have some striking magnetic properties. Among these properties are large saturation fields, H_s [1,2], and giant magnetoresistance, GMR [3]. When the Fe layers are about 30Å or less, each of these properties increases rapidly as the Cr layer thickness decreases below 30Å. Attempts to infer structural information from magnetic properties often lead to conflicting claims and two recent studies on GMR provide a classic illustration of this situation [4,5]. Despite the low X-ray contrast of Fe and Cr, quantitative experimental confirmation of the layered structure in actual samples is essential for experimental efforts to identify the cause(s) of rapid changes in H_s and GMR.

We have used anomalous dispersion enhancement of X-ray contrast to obtain structural data. The incoming X-ray beam was tuned between 7 to 17 eV below the onset of K-edge absorption in Cr. This procedure increased the contrast sufficiently to produce at least three low angle peaks and/or two satellite peaks in samples with layer thicknesses ranging from 8.2 to 50.8Å. These data were used in two ways. First, the number and locations of the peaks was sufficient to verify that the actual layer values matched nominal layer values to within one monolayer or less. Second, the intensities of the satellite peaks were compared to intensities predicted from an idealized model based upon (i) the anomalous corrections for Co and Fe and (ii) layers having an integral number of monolayers with flat interfaces. For samples having an Fe layer of 10.1Å, essential 5 monolayers, and Co layer thicknesses varying from 8.6 to 30.2Å, the experimental intensities initially approached the idealized model results as the Cr layer thickness increased and then decayed away as this layer thickness continued to increase. All intensities were normalized to the intensity of the average $\langle 110 \rangle$ line since orientational texture could cause a factor of three variation in absolute intensities. A more complete description of these findings has been published [6].

This work was done on line X7A at NSLS and the help of David Cox is gratefully acknowledged. Research support from the MSU-CFMR and The Research Corporation is also gratefully acknowledged.

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LATTICE INSTABILITIES IN La_2CuO_4 DOPED WITH A VARIETY OF RARE EARTHS

R. Harlow, M. Crawford, E. McCarron and W. Farneth (Du Pont)

La_2CuO_4 exists in a high-temperature tetragonal form (HTT, I4/mmm) in which the copper-oxygen sheets are, on average, perfectly planar and in a low-temperature orthorhombic form (LTO1, Bmab) in which the copper-oxygen octahedra tilt around one diagonal, (110), of the HTT cell by a few degrees. In previous experiments, we have noted that partial substitution of La with Nd leads to one or two additional phase transitions at low temperatures: $\text{LTO1} \rightarrow (\text{LTO2}, \text{Pccn}) \rightarrow (\text{LTT}, \text{P4}_2/\text{ncm})$. Small amounts of Nd in $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$ bring about the first transition; larger amounts, $x > 0.20$, are needed to induce the second phase transition. In the LTO2 and LTT forms, the octahedra tilt by unequal and equal amounts, respectively, about both diagonals of the HTT cell. We have now extended our studies to include a number of the smaller rare earth ions: Sm, Gd, and Dy. A diffraction pattern of a sample containing a 0.2 concentration of Nd is shown below and is compared with those from samples containing Sm and Gd at the same concentration. Nd only induces the $\text{LTO1} \rightarrow \text{LTO2}$ transition but the same concentration of Sm and Gd convert the structure to the LTT form, with Gd being more effective than Sm. Phase diagrams for Sm, Gd, and Dy have now been completed up to the limit of their solubilities and it can be generally concluded that the smaller the lanthanide ion, the greater is its ability to induce these additional phase transitions. Phrased another way, it takes less of the smaller ions to have the same effect.

THE CRYSTAL STRUCTURE OF A NEW FORM OF AlF_3 AS DETERMINED FROM ITS SYNCHROTRON POWDER-DIFFRACTION PATTERN.

Richard L. Harlow, Norman Herron and David L. Thorn (Du Pont)

Aluminum fluoride phases are established catalysts in many classes of fluorocarbon transformations. A new form of AlF_3 , the *theta* phase, was recently prepared by pyrolysis of a novel series of "organic" AlF_4 salts. This *theta* phase has been prepared in multigram quantities as a nearly pure material and has a diffraction pattern which indicates that it is highly crystalline. The synthetic route, i.e. thermal decomposition, strongly suggested that no single crystals of this phase would ever be forthcoming and so an *ab initio* structural study using powder data obtained at the NSLS was attempted. Although indexing the pattern was quite straightforward yielding a tetragonal unit cell with $a = 10.1844(1)$ and $c = 7.1728(1)$ Å, manual deconvolution of the highly overlapped peaks ($c = a/\sqrt{2}$, plus the presence of *eta*- AlF_3) was found to be necessary in order to correctly assign the intensities from each set of planes. The space group was clearly primitive and an n-glide perpendicular to the unique axis was indicated: space group $\text{P4}/\text{mmm}$ was thus assigned, but several others were possible. Attempts to solve the structure by Patterson techniques failed simply because there were four heavy atoms in the asymmetric unit. Direct methods eventually succeeded in solving the structure but only after some manual intervention in the phasing process. Refinement by Reitveld methods was straightforward. The structure is depicted in the figure and consists of corner-shared AlF_6 octahedra assembled into rings of 5, 4 and 3 Al atoms bridged by F. The 5-rings (a new structural motif for AlF_3 phases) form an undulating 3-D interconnected channel system around tetrahedral clusters consisting of 4-Al and 6-F atoms.

AB INITIO STRUCTURE SOLUTION OF Sn_3S_7 -PYRROLIDINE

J. A. Hriljac (BNL*), Y. Ko, and J. B. Parise (SUNY, Stony Brook)

A new tin sulfide was hydrothermally prepared in milligram quantities utilizing pyrrolidine as a structure directing agent. Powder diffraction data from 2 to 40° in 2θ were collected at $0.69986\text{\AA}$ at room temperature. Individual peak fitting to pseudo-Voigt line-shapes using a local least-squares routine gave a set of 33 accurately determined reflection positions. Auto-indexing with Visser's program ITO¹ led to a proposed C -centered monoclinic unit cell with $a = 19.256$, $b = 13.261$, $c = 8.568\text{\AA}$, and $\beta = 102.54^\circ$, and a figure of merit, M_{20} , of 49.4. The integrated intensities of ca. 1800 reflections (assuming space group $P2_1/m$) were extracted using Le Bail's procedure² and used as input into the structure solution package SHELXS-86³. The positions of two Sn atoms were inferred and subsequent difference Fourier techniques led to the location of an additional five S atoms. A second data set of higher quality was collected on a 0.3mm capillary sample at a wavelength of $1.20055\text{\AA}$ and this is currently being used for a Rietveld refinement in space group $C2/m$. The latest observed, calculated, and difference patterns are shown in the figure below.

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X7A

INTERCALATION OF HE IN C_{60} AT HIGH PRESSURES

A.P. Jephcoat (Oxford U.), J.A. Hriljac (BNL) and D.E. Cox (BNL)

X7A

The intercalation of molecular species into voids in the structure of solid C_{60} at the $\sim 1\%$ level is known to occur at ambient pressures and temperatures [1,2] and ^{13}C NMR techniques indicate that the diffusion of molecular oxygen and hydrogen into the octahedral interstitial sites of fcc C_{60} occurs readily (to occupancies as high as 50%) at pressures near 0.1 GPa (1 kbar) [1].

We have performed high-resolution powder x-ray diffraction measurements on compressed solid C_{60} in a variety of molecular pressure-transmitting media at 300 K as part of studies to determine the effect of pressure on the rotational ordering transition in C_{60} . The experiments were performed within a diamond-anvil cell to pressures near 14 GPa under fluid He and Ne, and with a methanol-ethanol (ME) medium to pressures near 2.0 GPa . Figure 1 shows a comparison of the pressure-volume data obtained in both media types. The ordering transition previously identified by the observation of superlattice reflections in the x-ray powder pattern of the sc phase [3] is clearly seen to occur near 0.4 GPa and is associated with a distinct ΔV when compressed in ME. The data obtained under fluid helium, however, show expanded volumes for the sc phase relative to the ME experiments, being $\sim 2\%$ larger at 0.4 GPa . It is likely that the difference is a direct result of negligible intercalation of the larger alcohols compared to a rapid diffusion of helium into the structure. Intercalated helium does not appear to expand the volume of the fcc phase at pressure and does not prevent the ordering transition at room temperature although other thermodynamic properties may be affected. The volume change observed in with ME medium is at least as large as the value predicted on the basis of existing calorimetric data as a function of pressure ($\sim 2.7\text{ cm}^3/\text{mol}$). Several runs performed with fluid and solid neon indicate that significant structural change occurs with increasing pressure.

Fig. 1. Pressure-volume data for compressed C_{60} with fluid helium medium (triangles) compared to methanol-ethanol (squares). Solid lines are 3rd-order Birch-Murnaghan fits to the equation of state for the sc phase above 0.4 GPa . Identical V_0 used in both fits ($427.35\text{ cm}^3/\text{mol}$, $a = 14.159\text{\AA}$).

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Research Council grant GR3/7984 (APJ); the Division of Materials Sciences, US Department of Energy, under contract DE-AC02-76CH00016(DEC, JAH).

Sample supplied by the University of Pennsylvania.

ANOMALOUS DISPERSION EFFECTS ON THE POWDER DIFFRACTION PATTERN OF THE RUBIDIUM ZINCOSILICATE MOLECULAR SIEVE VPI-9^{X7A}

Ralf Grosse Kunstleve, Lynne McCusker and Christian Baerlocher (ETH, Zurich, Switzerland)

A number of methods for structure determination from powder diffraction data have been developed recently, but the exploitation of anomalous dispersion effects has remained on the periphery. To investigate the feasibility of using such information for structure solution, the rubidium zincosilicate molecular sieve VPI-9¹, with two potential anomalous scatterers and an unknown framework topology, appeared to be an ideal case. With this in mind, three data sets were collected with $\lambda = 0.8164, 1.2831$ and $1.0198 \text{ \AA}$ (near the Rb and Zn edges and in between, respectively). Data evaluation is still in the early stages, but preliminary results are encouraging. The magnitude of the intensity differences at the three wavelengths can be seen clearly in the sections of data shown below.

Observed data collected near the Zn edge (top), near the Rb edge (bottom), and in between the two (middle). For comparison purposes, the 2θ scale has been normalized to $1.0 \text{ \AA}$ for all data sets.

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MU - PROGRAM FOR PLOTTING ABSORPTION EDGES FOR CHEMICAL COMPOUNDS

W. J. Marshall and R. L. Harlow (DuPont)

To aid in the selection of wavelengths using synchrotron radiation a VAX FORTRAN program has been written to calculate and graph the mass or linear absorption coefficient for a chemical compound vs. wavelength. The mass absorption values for each element are interpolated using Aitken's method in program FPRIME. To calculate the linear absorption coefficient the unit cell parameters and value of Z (units/cell) are required. The spectrum is then plotted using PGLOT graphics: An example is shown below. The program can be obtained by sending an email message to: MARSHAWJ@ESVAX.DNET.DUPONT.COM.

Subroutine to interpolate mass absorption at a point was taken from FPRIME. Originally written By Don T. Cromer. Joseph Calabrese was the author of the subroutines to interpret the chemical formula.

X-7A

Entrapment and Controlled Release of Xenon in Cd²⁺-Exchanged Zeolite Rho
J. B. Parise (CHPR and ESS, Stony Brook), J. Hriljac (Physics, BNL),
D. R. Corbin, L. Abrams, G. Jones and R. Harlow (DuPont)

Zeolite rho has been shown in the acid form to exhibit high activity and selectivity for the synthesis of dimethylamine from methanol and ammonia. Detailed structural characterization studies have also shown the aluminosilicate framework exhibits exceptional flexibility with particular sensitivity to cation, temperature, and degree of hydration. Structural studies of Cd²⁺-ion exchanged into zeolite rho showed a unit cell parameter intermediate to the extremes observed for this highly flexible framework with $a \sim 14.49 \text{ \AA}$; D-rho ($a = 15.0976(4) \text{ \AA}$, $Im3m$) and Ca,D-rho ($a = 13.9645(7) \text{ \AA}$, $I43m$) represent the extremes. More detailed studies and structure refinements indicated relocation of the Cd²⁺ ions from the 8-membered ring site to the 6-membered ring site in the framework of zeolite rho on heating from room temperature to 300°C or greater. As illustrated in Figure 1, the structural results show that below 300°C,

the pore opening is elliptical with Cd²⁺ blocking access to the internal surfaces of the zeolite. Above 300°C, the pore is essentially circular and is no longer blocked by cations thus allowing full access to the internal surfaces. We have demonstrated that we can take advantage of this unique flexibility to trap species,

specifically xenon, within the zeolite cages and controllably release them using Cd-rho.

Fourier difference map calculations based on synchrotron X-ray diffraction intensity measurements of the Xe-loaded Cd-rho sample collected at 13K, revealed density close to the double 8-ring (D8R) and single 6-ring (S6R) sites. The occupancy of 3.2 Cd at a site at $(x,0,0; x=0.6)$ corresponds well to the chemically analyzed value of 3.3 Cd/unit cell. The remainder of the scattering was assigned to Xe. Four sites were found: close to the D8R at $(x,0,0; x=0.5$ and $x=0.6)$ and close to the S6R sites at $(x,0,0; x=0.35$ and $x=0.2)$. The S6R sites are equally occupied by 0.75Xe and the D8R-site contains approximately 2.2Xe. The composition of the 8-ring sites is then $(Xe_2.2Cd_3.2)$, close to the maximum of six allowed. The total extra-framework scattering found is consistent with $(Cd_3.2Xe_3.7)$ per unit cell.

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X7A

STRUCTURAL STUDIES OF FULLERENES

G. B. M. Vaughan, P. A. Heiney, J. E. Fischer, A. R. McGhie, R. M. Strongin, M. A. Cichy, and A. B. Smith, III, U. Pennsylvania; A. L. Smith, Drexel U., D. E. Cox, BNL.

The thermal behavior of solid C₇₀ was studied using synchrotron x-ray powder diffraction and differential scanning calorimetry. The equilibrium solid state structures formed by C₇₀ were solved by full profile refinement techniques in which orientational and packing disorder were explicitly accounted for. Above 345 K, C₇₀ forms a plastic crystal, with an equilibrium face centered cubic structure. At lower temperatures, orientational freezing occurs in two stages. Between 295 and 345 K, disorder persists only about the long axis of the molecule, and the lattice undergoes a rhombohedral distortion. Below 295 K, the rhombohedral lattice undergoes a further distortion, resulting in a previous unobserved monoclinic structure, in which the molecules are presumed to be essentially static. The successive splittings of selected fcc lines are shown below: a) The fcc 311 and 222 peaks at 440 K. b) The same region in the (lower symmetry) rhombohedral phase at 300 K. c) The same region in the monoclinic phase at 15 K.

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CALCITIC SPONGE SPICULES: A RELATIONSHIP BETWEEN CRYSTAL TEXTURE AND SPICULE MORPHOLOGY

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Many groups of organisms use single calcite crystal - protein composites for constructing their skeletal elements. Here we report the results of our continuing research on the effects of anisotropic adsorption of proteins on crystal texture*, by studying differently shaped spicules of calcsponges. The morphological axes of each spicule bear a precise relation to the crystallographic axes of the constituent calcite. The shape of the monaxons, that have their *c*-axis coincident with the morphological axis (Fig. 1A), as well as the morphology of the planar triacts with their rays elongated along the *a**-axes (Fig. 2A), may reflect the tendency of calcite crystals to preferentially grow in directions that follow its three-fold symmetry. However, monaxons such as the one illustrated in Fig. 3A, bear no such relationship between crystallographic symmetry and macroscopic morphology. Proteins extracted from within such biogenic calcite crystals are able to affect morphology during growth *in vitro*, and their presence within the crystal influences its texture. This, therefore, raises the interesting question, whether there exists any relation between protein intercalation, revealed by the anisotropy in crystal textural properties, and the macroscopic morphology of the single crystalline skeletal elements.

A series of peak profiles in ω 2 θ mode were collected with a Ge(220) analyzer crystal. The measured peak widths do indeed reflect the anisotropy of the macroscopic morphology of the elements (Fig. 1-3). The coherence length is drastically reduced in the *c*-direction in the planar triacts (Fig. 2B,C) and the asymmetric monaxons (Fig. 3B,C), consistent with their growth perpendicular to the *c*-axis.

In contrast, the coherence length in the symmetrical monaxon is longer in the *c*-axis direction, in agreement with its morphology (Fig. 1). This is the first time that the textural anisotropy was also observed within sets of symmetry related reflections. The coherence length in the directions roughly parallel to the morphological axis of the asymmetric spicules is significantly larger than those in the symmetry related directions (Fig. 3B). These results show that there is a well defined relationship between crystal texture and morphology, and imply a very high degree of biological control over the process of spicule formation.

Figure. Schematic morphology-crystallography relationship (A) and the ω 2 θ profiles of the {0 2 4} set of reflections (B) and (0 0 12) reflection (C) for the symmetric *Sycon* slender monaxon (1), the planar *Clathrina* triact (2) and the asymmetric *Sycon* curved monaxon (3)

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*Berman A. *et al.* (1993) *Science*, 259, 776-779.

DIFFRACTION BY HIGH-PRESSURE-CELL DIAMONDS REGISTERED AS TRANSMISSION DIPS

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When experimentally determining the transmission of a high-pressure diamond-anvil cell of Malinowski¹ design by measuring the attenuation of the direct beam ($\lambda = 0.9204$ Å), we observed sharp dips in the intensity of the beam. The dips could be correlated with the events of diffraction by the diamonds². In Fig. 1 is shown the result from scans in ω ($\delta \omega = 1^\circ$; $0^\circ < \omega < 40^\circ$) at different χ -values ($\delta \chi = 2^\circ$; $0^\circ < \chi < 180^\circ$) with the detector at $2\theta = 0^\circ$. The DAC was mounted so that its axis remains along the direct beam when ω is held at zero and χ rotates through all settings.

For one value of $\chi = 2^\circ$, a single ω -scan was measured with 0.02° steps (Fig. 2) to show the sharpness of the dips. The inset shows detail of the local reduction of intensity due to the diffraction by the diamonds. The half width of the dips is consistent with the fact that the half width of the diffraction peaks of the diamonds is about 0.05° in ω .

The conclusion is, that one should avoid registration of sample reflections at angle settings giving diamond diffraction, viz. by choosing the proper azimuthal orientation of the sample diffraction plane.

1 M. Malinowski, J. Appl. Cryst. 20, 379 (1987).

2 S. Åsbrink, J. C. Hanson, A. Waskowska and I. Uszynski, High Pressure Research. Submitted.

Fig.1

Fig.2

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X7B

X-RAY CRYSTALLOGRAPHIC STUDIES OF ORIENTATIONAL ORDER IN SINGLE-CRYSTAL C_{60} AT 20K AND IN THE VICINITY OF $T_c=260K$

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We have collected extensive data sets on the low temperature (sc) phase of crystalline C_{60} in order to: a) verify and refine the crystallographic fits on powders taken by W. I. F. David and co-workers [1] and b) to extract an orientational number density and single particle potential from the un-mixed parity data set (the fcc reflections) in a manner analogous to that accomplished for the high temperature phase [2] at room temperature. We also wish to compare these room temperature results to those obtained just above T_c at 265K. The crystallographic fits below T_c will be done in collaboration with H. Bürgi and D. Schwarzenbach [3]. 727 peaks were measured above T_c at 265K while below T_c , 2300 peaks were measured at $T=256K$ and 720 peaks were measured at $T=20K$. This data is currently being reduced and corrected and will shortly be analyzed.

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X7B

A synchrotron X-ray powder diffraction study of $CoAl_2O_4$ and $CoGa_2O_4$ by PSD diffractometer technique.
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The samples of $CoAl_2O_4$ and $CoGa_2O_4$ were prepared hydrothermally from mixtures of freshly precipitated hydroxides of cobalt and aluminium, and of cobalt and gallium, respectively. The hydroxide mixtures were kept in ampouls of sterling silver in pressure vessels at 430°C and 50 to 80 MPa for 75 h, and the resulting blue oxide spinels were washed with water and dried in air. Synchrotron X-ray powder patterns were measured of the samples on a Huber diffractometer at the beam-line X7B at NSLS, Brookhaven National Laboratory. A curved INEL position sensitive detector covering 120° in 2θ , type CPS 120, was mounted on the 2θ -arm of the diffractometer. A Debye-Scherrer geometry was applied with the samples housed in 0.3 mm diameter Lindemann capillaries, which were kept spinning with a constant ϕ -rotation of two rpm to randomize the orientation of the crystals in the samples. The detector was calibrated using a sample of silicon ($a = 5.4305 \text{ \AA}$). This calibration gives the channel to angle relationship of the detector and the wavelength of the X-ray beam. The positions of the primary beam and the (111) reflections of Si were measured in a two degrees 2θ -stepscan with the detector, and the 58 sets of positions thus obtained were used to calculate a detector step vs. 2θ function by cubic interpolation. The diffraction patterns were then recalculated to equal step patterns using a cubic spline function. This gave a preliminary value of the wave length and the $\Delta 2\theta = 0.02885^\circ$ of the detector. The final wavelength $\lambda = 1.2033(1) \text{ \AA}$ was found in a profile refinement of a powder pattern of silicon. To obtain good counting statistics with the position sensitive detector counting times of a half to one hour were used.

The program DBW3.2S was used in the profile refinement. The full width at half maximum FWHM is given by $(U \tan^2\theta + V \tan\theta + W)^{1/2}$ and a pseudo-Voigt function was applied, given by $\eta \cdot L + (1-\eta) \cdot G$. L and G are the Lorentzian and Gaussian contributions to the reflections. η is calculated from the mixing parameters NA and NB as $\eta = NA + NB \cdot 2\theta$. No asymmetry parameters and preferred orientation parameters were applied.

The structures of the two spinels belong to the space group $Fd3m$ (No. 227). The sample of $CoAl_2O_4$ contained a minor impurity of $\gamma-AlOOH$, but in the profile refinement of the structure no positional parameters of the structure of $\gamma-AlOOH$ were refined. A considerable line broadening is observed for the two patterns. The hydrothermal preparation did thus not result in samples with large and well crystallized crystal grains. The profile refinement of the two structures indicated a considerable degree of inversion for the two spinels.

EXCITED-STATE YIELDS AND FLUORESCENCE STUDIES AT X7B

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A goal of fundamental radiation chemistry is to understand the interactions of ionizing radiation with matter and to determine the processes that follow the absorption of energetic photons. Absorption of X-rays in liquids leads to ions, electrons and excited states along the track of the photoelectrons ejected in the absorption events. The yields of excited states are predicted to decrease with decreasing X-ray energy.¹ A 27% excited singlet state yield decrease is predicted over the range 14 to 2 keV. This is a consequence of track effects which are of fundamental interest to radiation chemists. In the last run (Apr 93) excited singlet yields for *cis*- and *trans*-decalin were measured for X-ray energies from 5.5 to 14 keV. As expected the yields decrease with decreasing X-ray energy.

Porous silicon is produced when elemental silicon is chemically treated in an appropriate manner. When this remarkable material is irradiated with ultraviolet radiation, strong visible and near infrared light is generated. The mechanism by which the radiation is produced is the subject of intense experimental and theoretical investigations. The wavelength of the luminescence produced by UV radiation is characteristic of the particular chemical treatment used to produce the porous silicon. We have determined that irradiation of porous silicon samples with 3-10 keV X-rays produces luminescence similar to that generated by UV radiation. Using the X-ray ring running in single-bunch mode, we have observed that there is a component of the X-ray-induced luminescence from porous silicon that has a lifetime shorter than 1 nanosecond, perhaps as short as a few hundred picoseconds. Attempts are underway to measure the spectral distribution and lifetime of this luminescence more precisely.

¹W. M. Bartczak and A. Hummel, *J. Phys. Chem.*, in press.

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"INSTANT ZEOLITE" POWDER. IN SITU STUDIES OF ZEOLITE FORMATION AND THERMAL TRANSFORMATIONS USING POWDER DIFFRACTION.

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In-situ studies of chemical reactions and syntheses are of considerable interest in connection with investigations of reaction mechanisms as well as for optimization of synthesis conditions. The present investigation was performed in connection with development of an alternative route for the synthesis of zeolite Na-LTA for use in detergents. On-line syntheses of zeolite Na-LTA (zeolite 4A) were performed at various temperatures using time resolved powder diffraction (X7B) and a 120° INEL position sensitive detector. Crystallization delay (nucleation), digestion of amorphous material, crystallization and transformation of products is directly observable. Estimates of the progression of crystallinity and crystallite size as well as kinetic parameters may thereby be obtained. An example of the resulting diagrams is shown in Figure 1 with time along the z-axis. After an induction period zeolite LTA is formed, and after a short period the sodalite phase starts to crystallize. After a period of coexistence the zeolite phase disappears, and only the sodalite phase is visible. Digestion of the amorphous material was observed as a significant drop in the background during crystallization. The results clearly demonstrate that in situ powder diffraction using synchrotron radiation is a powerful tool for studying chemical reactions and syntheses as e.g. hydrothermal syntheses of zeolites.

Studies of thermal transformations and dehydration reactions were performed at temperatures up to 800°C. The thermally induced transformations of e.g. ion exchanged zeolites of RHO, NAT and ABW-type, "Zeolite N", layered titanium phosphates, lithium zinkphosphates and lanthanum manganites were studied. Figure 2 shows dehydration and thermal transformation of γ -titaniumphosphate, where a new partly dehydrated intermediate phase is observed.

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IN SITU STUDIES OF ZEOLITE DEHYDRATION USING POWDER DIFFRACTION

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The dehydration of the natural zeolite laumontite has been studied in situ from powder diffraction data collected at beam line X7B. The position sensitive detector used covers 120° in 2θ (CPS120 by INEL) and allows complete powder diffraction patterns, suitable for structure refinements with the Rietveld method, to be collected within minutes. The laumontite sample was contained in a 0.3 mm capillary and heated intermittently, 5 K/step and each pattern accumulated for 5 min.

Laumontite: 310 K, $\text{Ca}_4\text{Si}_6\text{Al}_6\text{O}_{48}\cdot 18\text{H}_2\text{O}$, C2/m, $Z=1$, $a=14.806(1)$, $b=13.1678(7)$, $c=7.5389(5)$ Å, $\beta=110.647(4)^\circ$. $R_p=4.8\%$, $R_w=2.0\%$ from 68 par. and 3637 obs. Laumontite contains four different waters: two Ca-coordinated (W2, W8) and two interstitial (W1, W5). The latter connect Ca-coordinated waters and framework oxygens through hydrogen bonding. In the initial dehydration steps, the interstitial waters (W1, W5) are expelled. On continued heating the Ca-coordinated W2 is also expelled, while the W5 site is partially repopulated. The unit cell volume is strongly correlated to the interstitial water site occupancies, and the partial repopulation of the W5 site causes an increase in unit cell volume despite the net decrease in water content. W8 appears almost unaffected by heating to 584 K, which ensures a minimum Ca-O coordination number of six.

Meta-laumontite: 584 K, $\text{Ca}_4\text{Si}_6\text{Al}_6\text{O}_{48}\cdot 8\text{H}_2\text{O}$, C2/m, $Z=1$, $a=14.5283(5)$, $b=13.1980(4)$, $c=7.4371(3)$ Å, $\beta=110.368(2)^\circ$. $R_p=5.3\%$, $R_w=2.2\%$ from 59 par. and 3637 obs.

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Temperature-dependent phase transitions from paraelectric α - TlInS_2 to ferroelectric β - TlInS_2

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The isotypic compounds α - TlInS_2 and α - TlGaSe_2 crystallize in the space group C2/c. For both phases two successive phase transitions occur (120 K and 110 K for TlGaSe_2 , 216 K and 197 K for TlInS_2) [1].

Neutron diffraction studies show that the structure of ferroelectric β - TlGaSe_2 is a superstructure of the paraelectric α -phase with a quadrupled c -axis. The modulation is caused by a shift of the Tl atoms out of the centers of the selenium trigonal prism.

Fig.1: The difference Δk between the wavevectors of the main structure reflection (3 3 1) and the superstructure reflection (3 3 3/4) is plotted against the temperature.

For TlInS_2 the nature of the intermediate incommensurate phase was investigated using the instrument on beamline X7B with its high resolution and wavelength variability. Several scans of reciprocal lattice rows along c^* were made. In the ferroelectric β -phase, ($T < 197$ K) superstructure reflections were recorded, which indicate a unit cell with $a = 10.899(3)$ Å, $b = 10.895(3)$ Å, $c_\beta = 4c_\alpha = 61.115(8)$ Å, $\beta = 100.61(3)^\circ$ at 147 K and the space group C2 (Nr. 5). The difference between the wavevectors of the main structure reflection (3 3 1) and the superstructure reflection (3 3 3/4) were determined at different temperatures (Fig.1). The wavevector for the reflection (3 3 3/4) in the temperature range from 197 to 216 K is superimposed on an incommensurate vector $\vec{q}_{ic}$. Its absolute value decreases with decreasing temperature and locks into the commensurate wavevector $\vec{k} = (0, 0, 1/4)$ at 197 K. Only the component of $\vec{q}_{ic}$ along c^* was measured.

For β - TlGaSe_2 it is known that the modulation along c^* is caused by small shifts of the Tl atoms in the (0 0 1)-plane. If β - TlInS_2 is isotypic to β - TlGaSe_2 , then, in general, the scattering contribution of the Tl atoms to the intensity of the superstructure reflections of the modulated phases will be greater than its contribution to the neighboring main structure reflections. Therefore, wavelength-dependent scans of several main- and superstructure reflections in the region of the Tl L_{III} -edge ($\lambda = 0.9793$ Å) were recorded. The smaller anomalous dispersion coefficient f' of the atomic form factor for thallium near the L_{III} -edge leads to different absorption behavior of the main- and superstructure reflections. This study was done, in order to show that: the thallium atoms are involved in the modulation of the incommensurate and commensurate low temperature structures.

In the future, a partial structure determination will be done using anomalous dispersion effects of the incommensurate phase.

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PHASE COEXISTENCE IN SINGLE CRYSTAL C₆₀ THROUGH ITS PHASE TRANSITION

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Above the first-order orientational phase transition temperature of $T_c=259.8\text{K}$, the C₆₀ molecules show hindered rotation in the fcc phase. Below T_c , these molecules form a simple cubic structure, accompanied by a sharp drop in lattice parameter. We have studied the structure of the sample in the temperature region in the vicinity of T_c . Starting with a virgin sample (never cooled below T_c) we have measured integrated intensities and radial scan profiles of the fundamental (046) reflection and 2 ordering reflections: the $(\bar{1}27)$, which is at a Q corresponding to $l=6$, and the $(0, 2, 13)$ which corresponds to the region where the $l=10$ component peaks, where the value of l indicates the index of the moments of the atomic distribution as expanded in spherical harmonics.

These measurements were repeated for 2 complete cooling and heating cycles. Because of variations in the incident beam intensity, normalization was done by periodically scanning a portion of the A1 (111) powder ring, from a small band of Al foil wrapped about the He-filled capillary housing the C₆₀ crystal. On the virgin cooling the sample transformed spontaneously and its mosaic spread increased from 0.02° to 0.15° . On all subsequent heatings and coolings we observed a coexistence region of several degrees over which both low and high temperature phases were measured as in Fig.1. The ordering reflections, however, showed only a very narrow hysteresis and we therefore tentatively ascribe the coexistence region not to hysteresis but rather to the cubic-to-cubic strain-induced stress.

Fig.1 Traces of the 046 reflection(s) showing coexistence of low (L) and high (H) temperature phases.

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PHOTOABSORPTION AND COMPTON SCATTERING IN THE DOUBLE TO SINGLE PHOTOIONIZATION RATIO OF He

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Double photoionization in He is of interest because the ejection of the second (shake-off) electron results from its correlation with the primary electron through the electron-electron interaction. Thus, calculation of the cross section for double photoionization is a good test of electron correlation models in atoms. Most theoretical studies have considered the photoabsorption process only and predict a high energy asymptotic limit of the ratio $R(h\nu)$ of the double to single ionization cross section of 1.66%. Previous measurements of $R(h\nu)$ have found an asymptotic limit of near 1.5%.¹ We have measured $R(h\nu)$ between 2.1 and 5.5 keV and the results are shown in the figure. Above ~ 3.7 keV we observe a fall-off in $R(h\nu)$ which we attribute to increased He⁺ production resulting from the onset of ionizing Compton scattering. The measurements are in fair agreement with a recent calculation by Andersson and Burgdorfer² which includes both photoabsorption and Compton scattering; however, the measured $R(h\nu)$ in the photoabsorption regime below ~ 3.5 keV is lower than the calculation by $\sim 0.4\%$. The effect of Compton scattering on $R(h\nu)$ can be approximately described with a simple model (dashed curve) which makes use of the Klein-Nishina Compton scattering cross section for free electrons and the constraint that the energy transferred to the H(1s) electron must be greater than the ionization potential.

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X8A

OPTICAL CONSTANTS AND SCATTERING FACTORS FROM REFLECTIVITY MEASUREMENTS: 50 eV TO 19 keV

R. L. Blake and J. C. Davis (LANL), D. E. Graessle and T. H. Burbine (Harvard/SAO), and E. M. Gullikson (LBL)

An improved reflection technique has been introduced to permit more accurate measurements of complex material optical constants δ and β , the density ρ , and from these the atomic scattering factors f' and f'' . Regions of normal and anomalous dispersion can be measured with resolving power 1000 or larger using a portable reflectometer that is moved to any of four beamlines at NSLS. Both the real and imaginary parts of the complex optical constants may be derived from fitting the Fresnel equations to measured reflectivity versus angle.

Measurements on X8A have provided the first determinations of δ and β for Ir, Pt, and Au over the M-edge regions (2000-3500 eV) and the L-edge region of Mo (2000-3000 eV). Surprisingly, the MIV and MV edges of Ir, Pt, and Au are found to be ~40 eV higher energy than electron spectroscopy binding energies. The Mo L-edges show no discrepancy, nor does the P K-edge for which we measured a classic "dispersion profile." There is some evidence of white line absorption on the MV and MIII edges in some of the x-ray spectroscopic data on Ir, Pt, and Au. In order for white line absorption to explain the difference in binding energy between x-ray and electron spectroscopies there would need to be some white lines on the MIV edges that we missed, and the final states of some white lines would be autoionizing to explain the electron spectroscopy results.

X8A

REFLECTANCE CALIBRATIONS OF AXAF MIRROR SAMPLES

D. E. Graessle, T. H. Burbine, J. C. Cobuzzi, E. M. Kellogg, and D. A. Schwartz (Harvard/SAO), R. L. Blake (LANL), and P. P. Gong (EG&G/EM)

A major long-term program is underway on X8 and U3 beamlines to calibrate the telescope mirrors of the Advanced X-ray Astronomy Facility (AXAF). This will be a national astronomy observatory under NASA sponsorship, to be launched into orbit in 1998. Witness flats evaporated simultaneously with the telescope mirrors will be evaluated at NSLS from 50 eV to 12 keV. Reflectivities are being measured versus energy at fixed grazing angles and versus angle at fixed energies. From the latter it is possible to derive the optical constants of the mirror materials. In turn, the optical constants can be used to calculate the reflectivity versus energy for comparison to the measurements. An auxiliary set of measurements, reported here, has been necessary to evaluate the consequences of mirror contamination; from oxygen during storage or carbon deposits that settle from vacuum systems or from the spacecraft. This molecular contamination study was carried out on Ir mirror samples; two of which were maintained as free as possible from contamination, one was inadvertently contaminated with carbon from storage in polyethylene containers, and one was deliberately coated with 110 Å of polyethylene after being measured as pure Ir. The presence or absence of hydrocarbon or oxygen contamination is readily detected by energy scans through the respective K-absorption edge regions. Calculated reflectivities including contamination layers may be used for quantitative analysis. Baseline measurements on U3C were adequate to verify the initial absence of contamination on the sample that subsequently acquired a carbon layer from the storage container. Baseline measurements on X8A were of very high quality that allowed us to explore sample differences with a sensitivity of 0.1 percent. We have shown that samples stored in Lexan or capran are not measurably contaminated in 12 months. Procedures established for storing, transfer, and measuring samples will be adequate for the AXAF mission requirements.

Polarization Dependence of X-Ray Photoelectron Yield of Au Photocathode

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The emission of photoelectrons from a plain photocathode excited by x-ray has been extensively studied for its vast applications (e.g. x-ray detectors and SEXFAS). Most work was done on measuring the total yield and the energy spectrum of photoelectrons excited by unpolarized light. The effect of polarized x rays has not been fully explored. Recently, it was reported¹ that the total photoyield of a gold photocathode is strongly dependent on the polarization state of the incident x ray in the 2-8 keV range. At a glancing incidence angle of 10°, the difference in photoyield between two polarization states normalized by their sum was measured to be as high as 50%.

We measured the total photoelectron yield of gold as a function of the incident x-ray polarization. Polarized x-rays with energies 2.5, 2.7 and 4 keV were used to excite a gold sample with the glancing incidence angle of x rays between 5° and 50°. We analyzed the spurious effects due to x-ray beam size and x-ray alignment precision at glancing incidence angle. The x-ray beam was aligned and limited in size accordingly by collimators to minimize these spurious effects that in some cases could mimic the real polarization signature. Contrary to the previous report¹, we found no measurable polarization dependence for all three x-ray energies. We conclude that the modulation factor, or the fractional change of the total yield when the polarization state is varied, is less than 4%. With the extensive use of synchrotron light, which is usually highly polarized, this effect could have some important implications for experiments measuring the total photoelectron yield, for example, in the SEXAFS studies.

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AXAF SYNCHROTRON CALIBRATIONS TESTING IN THE 5 TO 12 KEV PHOTON ENERGY RANGE

D.E. Graessle (SAO) and R.L. Blake (LANL)

The Smithsonian Astrophysical Observatory (SAO) Mission Support Team for NASA's Advanced X-ray Astrophysics Facility (AXAF) has completed another in a series of test experiment runs on Beamline X8C of NSLS. Reflectance and scattering measurements were conducted over the 5-12 keV photon energy range to test the quality of metal-coated flat mirrors as grazing incidence X-ray reflectors. Flats tested included two high-quality iridium-coated mirrors with differing roughness specifications, an iridium mirror intentionally contaminated with ~60Å polyethylene, and a control sample with the same type of Ir coating, but with no polyethylene layer.

Testing was also done (concurrently) of the horizontal alignment stability of the system a) within a given fill cycle, b) from fill to fill, and c) as a function of monochromator position along the rocking curve and as a function of energy.

Preliminary results indicate that horizontal alignment at a fixed energy within a typical fill cycle is quite adequate, giving reflectance results varying by less than 0.5 percent at the critical angle for iridium at 6400 eV.

From fill to fill it was found that some horizontal realignment of the reflectometer to the beam was necessary. This could be accomplished using the horizontal translating motors on the reflectometer positioning table. Systematic horizontal motion of the beam was found to occur as the energy was varied, which may be corrected in the future by adjusting the monochromator crystal alignment.

Scattering measurements were made from four mirrors at 8000 eV some of which will be compared to results from the same mirrors obtained from other laboratories. A surprisingly small difference was found in the scattering from a flat of 2Å roughness and one of 6Å roughness. Analysis of these data is in progress.

As part of our collaboration on optical constants through reflectivities, a sample of polycrystalline molybdenum was measured for reflectivity and scattering at 8018 eV, corresponding to the copper $K - \alpha$ line. This energy was chosen because it is expected that optical constants for molybdenum may be well known at this energy, which will allow for accurate determination of the sample surface microroughness. Analysis of the data is in progress.

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DETECTOR CROSS-CALIBRATION PROGRAM FOR 5 TO 20 keV PHOTONS

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The ongoing LANL/EG&G detector calibration program provides calibrated x-ray detectors and detector systems for x-ray experiments performed around the world. This past year EG&G used beam line X8C for two one-week calibration runs in March and July. Monochromatic photons from 5 to 20 keV were used to cross-calibrate a xenon filled ionization chamber sealed with beryllium windows, an ion chamber with diamond windows variously filled with nitrogen at 750 torr and argon at 400 and 760 torr, several silicon photodiodes from IRD (International Radiation Detectors company) one of which was previously calibrated by NIST at lower photon energies, silicon photodiodes from Smithsonian Astrophysical Observatory, and a tantalum photocathode beryllium windowed high-flux x-ray diode. The calibrations were done using an IBM-PC based computer program which sets the monochromator, reads the beam line parameters, takes background noise readings, reads detector output, calculates detector response and error bars, logs the data and displays the calibration as the data is being taken. Results of the calibration runs yielded absolutely calibrated detectors with error bars of less than 10 %.

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EXAFS Studies of Copper-Containing Monooxygenases

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Abstract. Further studies have been carried out to characterize the structure of the catalytic centers in copper monooxygenase enzymes and inorganic model systems. Progress has been made in determining the individual coordination at each of the copper sites which comprise the active center in dopamine- β -hydroxylase. Derivatives of the Cu(I) form of DBH have been made in which Cu_A, the electron transfer site, has been selectively removed, allowing Cu_B, the O₂-binding center to be studied by EXAFS. The sites differ in that only Cu_B is able to bind CO. Cu_B has been found to be coordinated to 2 histidines and a S-donor ligand, whilst Cu_A appears to be coordinated to 3 histidines (by inference from previous published data on the fully metallated enzyme). Further characterization of the Cu(I) centers is proceeding via the preparation and characterization of isocyanide complexes. Infra red studies have established that in contrast to CO, isocyanides apparently bind to both coppers but differ in their IR stretching frequencies, again suggesting structural inequivalence. As a prelude to full characterization of the DBH-isocyanide system, complex formation between deoxyhemocyanin and 2,6-dimethylphenyl isocyanide (DIMPI) has been studied. One DIMPI has been found to bind at each copper center in Hc, and the EXAFS of this complex has been measured but not yet fully analyzed. EXAFS studies have also been carried out on the complex formed between $[\{\text{Cu}(\text{TMPA})\}_2(\text{O}_2)]^{2+}$ and Fe(III)tetraphenylporphyrin, an important model for the metal centers in cytochrome-c-oxidase. The EXAFS analysis predicted the presence of a μ -oxo-bridged Cu-O-Fe unit with Cu-O=1.82 Å, Fe-O=1.72 Å, Cu-Fe=3.53 Å and the Cu-O-Fe angle 170°. The accuracy of this structure has recently been confirmed by a high-resolution crystal structure.

Blackburn, N. J.; in *Bioinorganic Chemistry of Copper*, Karlin, K. D.; Tyeklar, Z.; eds., Chapman & Hall, New York, 1993, 164-179.

XAFS, POLARIZED XAFS, AND DAFS STUDIES OF METALLOPROTEINS AND MODEL COMPLEXES

Grant Bunker, Habib Moltaji (Physics Department, Illinois Institute of Technology, Chicago IL), Ke Zhang (Biostructures Institute, Univ. City Science Center, Philadelphia PA)

We have continued our ongoing studies of the structure of metalloproteins, principally ribonucleotide reductase and model complexes, with the aim of evaluating the suitability of the FEFF5 program, which represents the state of the art for ab initio theoretical XAFS calculations. For several years we have been working toward full fitting of enzyme data including multiple scattering and thermal disorder, and the FEFF series of programs constructs sufficiently accurate potentials that at last theoretical "standards" are comparable in accuracy to experimental ones. Initial results are encouraging but the parameter to data ratio continues to be an issue and we are exploring several approaches to address this fundamental problem.

We have also conducted initial tests on single crystalline films of Cu phthalocyanine and other compounds to explore the feasibility of performing Diffraction Anomalous Fine Structure (DAFS) experiments on beamline X9B, and to try to assess the effects of anisotropy of the anomalous scattering in DAFS (corresponding to dichroism in XAFS), which should be important for planar complexes such as hemes. DAFS offers the potential for site selective XAFS and for performing XAFS on complex mixtures of crystalline phases. We expect it will be most useful in biology for synthetic multilayer biological structures such as proteins in LB films, and biominerals. The results of our initial experiments are that DAFS experiments are indeed feasible using the standard beamline equipment and XDC software through the use of specially written beamline control scripts. We have not had much success with powders, however. To date the data are not of adequate quality for detailed data analysis, but it seems clear that the forthcoming version of XDC with an extended beamline control scripting language (available late '93 or early '94) and improvements to goniometry and detectors should make DAFS practical on beamline X9B.

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KINETICS AND MECHANISM OF LIPID PHASE TRANSITIONS Martin Caffrey (Ohio State U.)

Vital biological dynamic processes such as membrane fusion and fat digestion involve changes in lipid phase state. A knowledge of the kinetics and mechanism of lipid phase transitions is integral to our understanding of the structure and composition requirements of transitions that occur in biological, model and reconstituted systems. We use time-resolved x-ray diffraction (TRXRD) to study such processes and our current focus has been the development of pressure-perturbation methods, in conjunction with TRXRD, as a convenient way of triggering the transitions. Measurements made at NSLS this past year indicate that the pressure-oscillation approach is working and that useful kinetic data can be collected. Our objective for the coming year is to refine these new instrumentation and data collection methods with a view to establishing the kinetics and mechanism of the chain-melting transition in model biological membranes.

In conjunction with the kinetic measurements, the following equilibrium study was performed. The pressure-temperature phase diagram of phosphatidylethanolamine in 50 % (w/w) water was constructed in the range of 1 to 1,200 bar and 65 to 90 °C. Measurements were made using synchrotron-based x-ray diffraction in samples contained in a high pressure beryllium cell. The pressure dependence of the lamellar chain-melting ($L_{\beta'}/L_{\alpha}$) transition temperature, dP/dT_m , was determined to be 41 ± 1 bar/°C. The pressure dependence of the lamellar repeat distance at constant temperature, $(\partial d/\partial P)_T$, in the L_{α} and $L_{\beta'}$ phases is 3.0 ± 0.5 and 1.2 ± 0.2 Å/kbar, respectively, and -0.11 ± 0.01 Å/kbar for the chain packing repeat in the $L_{\beta'}$ phase. These values are insensitive to temperature in the range studied. The lamellar repeat and acyl chain spacing in the gel phase increase linearly with temperature at a given pressure. The corresponding slope values, $(\partial d/\partial T)_P$, are 0.11 ± 0.02 and 0.0042 ± 0.0003 Å/°C, respectively, and do not change with pressure in the range studied.

Other projects in progress include: 1) Phase identification and structure characterization of C15:1c10 monoacylglycerol/water system for T-C phase diagram construction in the range 50 - 95 °C. 2) A study of the effect of biologically active peptides on the phase properties of hydrated lipids with a propensity to form nonlamellar phases. 3) Mesophase structure measurements related to curvature energy calculations.

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TIME RESOLVED X-RAY SPECTROSCOPY STUDIES USING A 13-CHANNEL TIME-BASED DISCRIMINATOR

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The Canberra germanium detector produces current pulses where the amount of current is related to the energy of the incoming x-ray photons. The pre-amplifier receives the charge impulses (Q_m) from the detector and stores an equivalent charge on the feedback capacitor (C_f). A step function with voltage $V_o = Q_m/C_f$ is produced, where the pulse height is related to the original energy of the x-ray pulse. We used the unipolar outputs from the existing Canberra spectroscopy amplifiers of the 13-element detector setup at NSLS beamline X-9B as an input to a multi-channel (maximum 14) discriminator/time-base circuit.

The boards sample the pulse heights and reject pulses not matching the user specified window. Discriminated pulses are partitioned into specified time bins under software control. The software allows the user to specify the width of the time bins, in this case from 5 μ s to 300 ms width per bin. 2048 bins are available so that a kinetic scan may last from 10 ms to 10 minutes. All channels begin data acquisition at the same time triggered by a TTL level pulse, the user may specify up to 65,000 triggering events that may be co-added, with a maximum count rate of 65,000 counts per bin (16-bit).

The following experiment was performed with approximately 10^{12} photons incident per second. In order to prevent saturation of the energy resolving germanium detector, a Soller slit assembly was designed and used with a fluorescence filter. This configuration achieved an N_{ph} of over 2×10^5 counts per second using a 2 mM cobalt sample in a flow cell. The figures show x-ray edge spectra collected using the 13-channel time-resolved discriminator circuit and a non-time resolved experiment to show the comparability of signal to noise. The total counting time is 1 sec per point in each case. For the time-resolved experiment this was 1 ms time bins with 1000 triggers averaged. At a 20 Hz repetition rate, the entire data collection required 1 hour. Overall, the comparison is excellent, and the signal to noise is outstanding. Since this experiment was performed at 150 ma current improvements are possible. This shows the feasibility for time-resolved spectroscopy for repeatable triggered events using a step-scan procedure. This work was supported by NSF-BIR-#9317769

A C₆₀ MONOLAYER TETHERED TO THE SURFACE OF AN INORGANIC SUBSTRATE: ASSEMBLY AND STRUCTURE

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The "fullerene" C₆₀ has been tethered to a silicon oxide surface via formation of a (pyridyl)_n-OsO₄-C₆₀ coordination complex utilizing the pyridyl endgroups of a pyridyl-terminated, self-assembled organic monolayer chemisorbed on the substrate. The step-wise fabrication of the tethered C₆₀ monolayer was monitored qualitatively by UV/vis absorption spectroscopy and firmly established via its profile structure determined by high-resolution x-ray interferometry/holography, utilizing Ge/Si multilayer substrates fabricated by molecular beam epitaxy. Preliminary high-resolution x-ray diffraction results suggest that the in-plane structure of the tethered C₆₀ monolayer consists of a primitive, planar hexagonal lattice of C₆₀ ($a_{C60} \cong 12\text{\AA}$, correlation length $< 50\text{\AA}$), epitaxial 2x2 on the underlying planar hexagonal lattice of the pyridyl-terminated self-assembled monolayer ($a_{pyr} \cong 6\text{\AA}$, correlation length $\cong 400\text{\AA}$) and centered $9 \pm 1\text{\AA}$ above the pyridyl-endgroups.

A preliminary version of this work has been published in the Journal of the American Chemical Society, 1993, Vol. 115, p. 4383 and was supported by the National Science Foundation (NSF) Materials Research Laboratories (MRL) Project under Grant No. DMR-91-20668 and the National Institutes of Health (NIH) Grants GM-33525 and RR01633.

DISCOTIC LIQUID CRYSTALS

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We used high resolution powder x-ray diffraction together with differential scanning calorimetry to establish the phase diagram, liquid crystalline structure, and crystalline structure of a series of hexa-*n*-alkylthiotriphenylenes. At least nine crystal phases are observed. The helical pitch seen in the helical phase is incommensurate with the molecular spacing when measured in single-orientation strands, while commensurate in powder samples.

Phthalocyanines are synthetic analogues of porphyrins that are of interest because of their electrical, optical, and catalytic properties; some are commercial pigments and catalysts. In an effort to understand the effect of chain branching and choice of heavy metal atom on structure and liquid crystalline properties, we used powder x-ray diffraction to study a series of branched chain octa-(2-ethylhexyloxy) Pt and Pb phthalocyanines. We find that a typical Pb phthalocyanine had a square discotic columnar phase, while a Pt phthalocyanine had an oblique discotic phase.

TIME DEPENDENT X-RAY DIFFRACTION STUDIES OF MUSCLES FOLLOWING LASER TEMPERATURE JUMPS

James A. McCray, Quangning Yang, Zhi Cai (Drexel University), and Gerold Rosenbaum (University City Science Center)

Elucidation of the chemical-physical mechanism of muscle contraction has been a long sought after goal. This research combines laser induced temperature jumps of muscle fibers and time-resolved low angle X-ray diffraction in order to determine which steps in the muscle cross-bridge cycle are temperature-sensitive and thus to be able to study their properties. This method is particularly applicable to the study of conformational changes because conformational equilibria are usually temperature sensitive. Attached and detached states may be studied by this technique.

During both the October 1992 and June 1993 runs steady state diffraction patterns were taken with monochromatic radiation and image plates of chemically skinned bundles of 12 fibers of rabbit psoas muscle at temperatures ranging from 4.9°C to 25.0°C in roughly 5°C intervals for fibers in relaxed and rigor solutions. X-ray intensities at various steady temperatures must be determined first before time-dependent low angle X-ray diffraction following laser temperature jumps can be attempted. Tension transients following laser temperature jumps have been found but correlation with transient X-ray intensity changes is needed to determine if the changes are associated with cross-bridge binding or conformational changes.

The X-ray intensity data for relaxed fibers is being analyzed on a Macintosh LC III computer with the analysis program, Image 1.33g. Meridional reflection intensities have been analyzed in order to determine their temperature sensitivities. It has been found that between 5 and 25 °C the intensity of the 14.3 nm reflection does not change very much while the 21.4 nm reflection is highly temperature sensitive.

Measurement of the intensities of low angle X-diffraction patterns as a function of time following sudden temperature perturbations combined with knowledge of the hexagonal lattice structure of the thick and thin filaments in the myofibril and helical structure of the actin, tropomyosin and myosin filaments allows determination of the rate constants involved in cross-bridge binding and conformational changes. This information will lead to a better understanding of the molecular details of the conversion of chemical to mechanical energy in the muscle contraction process.

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X9B

X-Ray Edge Structural Holeburning of Carbonmonoxymyoglobin (MbCO)

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Carbonmonoxymyoglobin (MbCO) has been shown to have various conformational substates that bind carbon monoxide at different rates. The structures of these substates and the intermediates involved in the process of ligand binding to myoglobin are poorly understood. However, x-ray absorption spectroscopy is an excellent technique for directly examining the heme environment of these intermediates. The position of the x-ray edge provides information on the iron charge density, which changes upon ligand-binding.

We photolyzed carbon monoxide from myoglobin at cryogenic temperatures to obtain an x-ray absorption spectrum of the MbCO photoproduct (Fig. 1). The photoproduct shows a shift of the x-ray edge position to a lower energy, this trend is consistent with a "deoxy-like" character. The sample is warmed in small increments, allowing the sample to progressively recombine, and x-ray absorption spectra are taken at each temperature. Each spectrum represents a particular distribution of MbCO structural intermediates, i.e. a temperature-dependent fraction of bound and unbound MbCO molecules.

By subtracting a fully recombined spectrum from each partially recombined spectrum ($\text{Mb}^*\text{CO} - \text{MbCO}$), a difference spectrum is obtained. Doing so removes any contribution from the recombined MbCO molecules, leaving only structural characteristics of the remaining photoproduct distribution (Fig. 2). As expected, the largest difference in the x-ray edge position occurs at the lowest temperature, where the fraction of photoproduct is greatest. As the sample warms and thus recombines, this difference decreases and, interestingly, the position of the photoproduct distribution maximum also shifts to lower energy. This is evidence for "structural holeburning." In other words, the part of the photoproduct distribution that has a higher barrier to recombination (i.e. recombines at a higher temperature), is more "deoxy-like" in character, indicated by an x-ray edge position at a lower energy. These structural holeburning results provide direct evidence for the presence of multiple intermediate states involved in carbon monoxide binding to myoglobin. This work was supported by the NIH grant #HL-45892.

Figure 1

Figure 2

X9B

THE EFFECT OF TEMPERATURE ON THE PROFILE AND IN-PLANE STRUCTURES OF ALKYL-SILOXANE SELF-ASSEMBLED MONOLAYERS ON SiO_2 SUBSTRATES VIA X-RAY INTERFEROMETRY/HOLOGRAPHY

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X-ray Interferometry was used to study the profile structures of annealed C16 alkylsiloxane self-assembled monolayer (SAM) films chemisorbed on germanium/silicon (Ge/Si) multilayer substrates fabricated by molecular beam epitaxy (MBE). First, a model refinement analysis of the meridional X-ray diffraction from the bare Ge/Si multilayer substrates was performed, based on the MBE fabrication specifications, to determine their relative electron density profile structures. Second, a highly constrained, real-space refinement analysis, employing the thereby known profile structure of the Ge/Si multilayer substrate plus the organic overlayer for each SAM from their respective meridional X-ray diffraction. Last, a real-space refinement analysis was used to determine the absolute electron density profiles of the inorganic multilayer-organic overlayer structures. Two cases of C16 SAMs were investigated. The first C16 SAM was annealed two weeks after preparation while the second C16 SAM was annealed within a few hours of preparation. For the first case, the absolute electron density profiles demonstrate that the alkyl chains have a tilt angle of approximately $32 \pm 3^\circ$ and have an electron density of $0.30 \pm 0.01 \text{ e}/\text{\AA}^3$. The absolute electron density profiles did not vary over the temperature range studied ($22^\circ\text{--}90^\circ\text{C}$) indicating that if the SAM is well ordered initially, then its absolute electron density profile does not vary with increasing temperature or over time. For the second case, the absolute electron density profiles demonstrate that the alkyl chains are initially less ordered at room temperature, become more ordered with increasing temperatures, and return to their initial less ordered state upon a decrease to room temperature. Upon examination of this same freshly prepared C16 SAM case one week later at room temperature, the absolute electron density profile had evolved further to a more ordered structure, similar to the ordered high temperature structure. The alkyl chains are tilted approximately $37.5 \pm 3^\circ$ from the surface normal and have an electron density of $0.30 \pm 0.01 \text{ e}/\text{\AA}^3$, similar to the first case tilt and density of the initially well ordered C16 SAM. Both ends of the self-assembled chain, the SiO_2/SAM and CH_3/He interfaces, ordered with increasing temperature and over time. The so-derived electron density profiles were proven to be correct by X-ray holography where, under appropriate conditions, the profile structure of the organic overlayer is contained explicitly in a specific region of the Patterson function, derived uniquely from the meridional X-ray diffraction data from the inorganic multilayer-organic overlayer without phase information or model parameters. The profile and in-plane structures for both annealed C16 SAMs are consistent with the previously found structures of a well ordered C16 SAM at room temperature.^[1] Studies of the evolution of the in-plane structures of these SAMs during this annealing process are currently being investigated.

[1] Xu, S.; Fischetti, R. F.; Blasie, J. K.; Peticolas, L. J.; Bean, J. C. *J. Phys. Chem.* **1993**, *97*, 1961.

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A LOW ANGLE DIFFRACTION INVESTIGATION OF THE THIN FILAMENT STRUCTURAL CHANGE THAT REGULATES MUSCLE CONTRACTION.

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Muscle force or shortening is powered by the cyclical interaction of myosin crossbridges with the actin filament as they split ATP. With skeletal muscle myosin this reaction proceeds unhindered if the actin filament associated regulatory proteins troponin and tropomyosin are absent. When present they inhibit strongly-binding interactions of the crossbridges with actin, essential for ATP product release from the enzyme, thus inhibiting active cross-bridge cycling. The addition of calcium to this system releases the inhibition. Calcium ions bind to troponin and it has been proposed that this influences the position of the tropomyosin thus unblocking the cross-bridge binding sites. Tropomyosin is a filamentous coiled coil molecule which lies along the actin filament and overlaps head to tail with neighbouring molecules along the thin filament (actin plus regulatory proteins). Low angle x-ray diffraction data taken following the excitation of living frog fibres showed that there was a very rapid change in the thin filament fibre diffraction pattern, occurring before cross-bridge attachment. The change suggested an azimuthal rearrangement of the mass of the thin filament to give a more 4-stranded appearance; a rotation of the tropomyosin into the groove of the actin helix would produce such a change (Haselgrove, Cold Spring Harbour Symp. Quant Biol. 37, 341, 1972).

Since then the problem has been to provide convincing structural evidence for this mechanism of regulation. It is only recently that x-ray patterns from actin filaments have been fitted by an atomic model of actin (Holmes et. al Nature, 1990, Lorenz et. al. JMB, 1993 in press). Using the Holmes atomic model, diffraction data from oriented actin-tropomyosin gels taken at the BNL last year have been used to model the position of tropomyosin on the filament (Lorenz, Popp & Holmes, in preparation). This is in the absence of troponin and is a calcium insensitive system which is capable of binding cross-bridges and the fit to the diffraction data is consistent with this since the tropomyosin lies away from the myosin binding residues on actin.

Obtaining diffraction data from the fully regulated thin filament has proved more difficult. The presence of troponin appears to disturb the orientation of the filaments in the gel, so instead, in the last round of experiments at the NSLS, we used skinned rabbit psoas fibres pulled out so that the thick and thin filaments no longer overlap. The helical diffraction from the myosin head arrangement was disordered by removing ATP from the system leaving predominantly the thin filament pattern. Using the fine focus from the mirror/monochromator camera of X9B, a camera length of 40cm and the Fuji imaging plate detector we obtained diffraction patterns from regulated thin filaments in the off state and in the presence of varying amounts of calcium. The results show very clear and substantial intensity changes on the 1st and 2nd actin layer lines which can only be accounted for by a large (ca. 25°) azimuthal rotation of the tropomyosin strand around the actin filament. The modeled off-state position of tropomyosin covers a number of known myosin binding residues of actin and would sterically block cross-bridge attachment. There is also a small increase on the 6th actin layer line which implies that some change takes place in the actin monomer itself as tropomyosin shifts position but the model has yet to be refined against this data. The titration of the structural change against calcium ion concentration shows that the transition occurs at a higher calcium concentration and is sharper than the force dependence of this muscle on calcium.

STRUCTURE OF THE BINUCLEAR ACTIVE SITE OF THE QUINOL-OXIDIZING aa3 FROM *BACILLUS SUBTILIS*

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Cytochrome aa₃-600 is a terminal quinol oxidase of *Bacillus Subtilis*, which belongs to the large family of structurally and functionally related respiratory enzymes to which mitochondrial cytochrome c oxidase also belongs. However, the Cu_A center typical of the cytochrome c oxidases is lacking from cytochrome aa₃-600. The presence of only one copper, viz. Cu_B of the binuclear heme iron-copper site, makes cytochrome aa₃-600 especially suitable for XAS analysis of this structure. Cu and Fe XAS data for fully oxidized cytochrome aa₃-600 indicate a structure for the binuclear site similar to that previously reported for mitochondrial cytochrome c oxidase (see Powers et al. [1981] Biophys. J. 34, 465-468). Heme Fea₃ has a proximal histidine nitrogen ligand 2.1 ± 0.02 Å from the iron, and a distal S or Cl ligand at 2.36 ± 0.03 Å. The latter is also a ligand of Cu_B (2.21 ± 0.02 Å), and apparently forms a bridge between the two metals which are 3.70 ± 0.06 Å apart. Cu_B has two more close-lying ligands at 1.95 ± 0.02 Å, which are likely histidine nitrogens. The similarity between EXAFS of Cu_B and type 1 "blue" copper is contrasted to EPR and optical spectroscopic properties of Cu_B, and the nature of the bridging ligand is discussed.

HEMEPROTEIN CATALYSIS: STRUCTURE FUNCTION RELATIONSHIP

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The peroxidases and the oxygen transport proteins both contain an active site consisting of a single iron-heme with a proximal histidine ligand. Unlike the oxygen transport proteins, however, the peroxidases are capable of catalyzing the oxidation of substrates having very high redox potentials. How can this same structure perform these two radically different functions? X-ray absorption spectroscopy has been used to compare the iron-heme active site structures of several peroxidases [plant, fungal, bacterial, and mammalian] with those of the oxygen transport proteins and models. The distinguishing feature is the iron to proximal histidine distance which is ~ 0.2 Å shorter for the peroxidases. This results in a longer iron to pyrrole nitrogen average distance [Fe-N_P] in the heme of peroxidases. Significant differences are also found in the Fe-N_P distances among the various peroxidases. Preliminary data suggest that the reactivity of the peroxidases with various substrates is correlated to the Fe-N_P distances in just the opposite way as that found for the oxygen transport proteins.

EXAFS STUDIES OF UTEROFERRIN AND ITS ANION COMPLEXES

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Our EXAFS analysis suggests the presence of a hydroxo- or alkoxo-bridged diiron unit also supported by a carboxylate bridge in the mixed-valent active form of uteroferrin (Uf). It is proposed that tyrosine and histidine are terminal ligands to the Fe(III) center in Uf_r, and histidine and the chelated carboxylate coordinate to the Fe(II) center, with solvent molecules completing the diiron coordination sphere. The diiron cores of Uf_o•PO₄ and Uf_o•AsO₄ are significantly different from that of Uf_r, with much shorter iron-iron distances, and the tetraoxo anion inhibitors bridging the diiron core in a bidentate fashion. The structural information derived from this study reveals a slightly modified active site from that found for the R2 of ribonucleotide reductase from *E. coli* and suggested for the hydroxylase component of methane monooxygenase.

Fig 1:A) $k^3\chi$ Fourier-filtered and B) fourier-transformed $k^3\chi$ EXAFS data (x) and simulations(-) of Uf samples.

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STOPPED FLOW-EXAFS STUDIES OF ENZYME INTERMEDIATES

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In order to study the structures of enzyme intermediates(1), we have been developing the Rapid mixing, Freeze-quench and Flash photolysis techniques in combination with X-ray absorption spectroscopy. The stopped flow-EXAFS unit which we have developed recently was able to operate between -10 to 30°C with 5msec. dead time. Using this unit, we have studied number inorganic model reactions with EXAFS at 20 to 25mM metal concentrations(2). Though the stopped flow system takes 80ul per shot, because of detection limitations of X-ray fluorescence photons and long average times to collect EXAFS spectrum, it becomes almost impossible to collect reasonable EXAFS data with enzymes. For example, it takes 2000 shots of stopped flow (150ml) of 3mM hemoglobin and H₂O₂ to get a single XAF spectrum of Ferryl intermediate of hemoglobin. In view of this, we have modified our Stopped flow system to do Cryo-stopped flow experiments. The unit also has the fiber optic coupling to the EXAFS observation cell so that the on-line optical spectrum of the intermediate could be measured by using dual wavelength spectroscopy unit at the beam line. This method utilizes the fact that different steps in the enzyme catalyzed reactions involve different free energies and enthalpy of activation. The samples could be mixed at -50 to -70°C in a suitable organic solvent for a given enzyme. The enzyme intermediates could be sequentially generated and quenched by increasing or decreasing the temperature of the EXAFS observation cell. This method is ideally suited for EXAFS with occupancy and long life time of the intermediate. With this setup, we were able to get excellent signal to noise EXAFS spectrum with 1.2mM Ferryl myoglobin(Fig 1), and 2mM carboxy peptidase(200ul) sample at -50 and -20°C. We have also made peroxidase compound-I in this unit at -50°C, but this intermediate has been observed to decompose quickly in presence of X-rays at -50°C in buffer-DMF solvent system.

fig1. Exafs spectra of metmyoglobin and ferrylmyoglobin and the difference spectra in stopped flow cell

fig2. Optical spectra of myoglobin and ferryl myoglobin at -30°C in stopped flow cell

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X-RAY DAMAGE MECHANISMS AND POSSIBLE WAYS TO PROTECT THE PROTEINS DURING EXAFS STUDIES

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The primary radiolytic products of X and γ-ray irradiation of the proteins in absence of O₂ are same but the relative amounts of these species differ with energy(eq.1).

We have investigated the radiation induced changes on number of metallo-proteins(2) with white X-ray beam in X-9B, with monochromatic(7.5 KeV) in X-9A and with Cobalt source at U. of Penn. These studies indicated that the mechanisms of radiation induced changes to the proteins are different with different sources. In the presence of O₂ superoxide ion has found to reduce and damage the heme proteins. Whereas in the absence of O₂, the direct damage of protein in concentrated samples and indirect damage from the radiolytic products of water and buffer dominates the damage to the proteins.

The following general guidelines are useful for protecting proteins during X-ray spectroscopic studies. Use of low temperatures(<100K)(1, 2), removal of oxygen from the sample and addition of free radical scavengers. Cr(NTA), Glycerol, DMSO, Cysteamine and catalase gave various levels of protection during the irradiation. The Cr(NTA) complex has been found to be effective protecting agent in number of heme protein irradiation studies. We are presently evaluating its use in stabilizing the ferryl intermediates of heme proteins in presence of X&γ-rays.

Fig. 1). Optical spectral changes in myoglobin during X-ray irradiation at X-9A in focused beam at 77K.

Fig. 2). Effect of Cobalt(Co-60) γ-radiation on myoglobin in absence of O₂ at room temperature.

Fig. 3). Pre edge and near edge X-ray absorption structural changes in Ferryl myoglobin during EXAFS data acquisition at X-9B at -40°C

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Time-Resolved X-ray Spectroscopy of Coenzyme B-12 Cofactors

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Methylcobalamin dependent enzymes catalyze methylation reactions which are accompanied by cyclization of the cofactor between Co(I) and Co(III)-methyl states. We chose to study the structure of the five coordinate "base-off" species, where the 5,6-dimethylbenzimidazole ligand in the fifth position is detached. Our earlier time-resolved nanosecond optical studies at room temperature have uncovered some unusual features of the "base-off" photoproduct, implying the presence of a four coordinate (square planar) complex subsequent to the photolysis of "base-off" alkylcobalamins. Such four coordinate Co(II) species are expected to be unstable but their relevance to B-12 enzyme mechanisms is highlighted by our recent discovery of a four coordinate Co(II) species in the corrinoid protein of *C. thermoaceticum*.

We utilized the time-multiplexed laser-photolysis system coupled to a rapid flow cell in order to characterize the structure of the initial photoproduct. Figure 1 shows the pre-edge spectra of the CW "base-off" 5-coordinate methylcobalamin and the 4-coordinate Co(II) species from *C. thermoaceticum*. The difference between the 1s-3d peak of 5-coordinate species and the 1s-4p+SD peak of the 4-coordinate species can be seen clearly. Since the quantum yield of the "base-off" species is 0.4, the production of a square planar photoproduct should reduce the intensity of this transition by 40% coincident with the laser flash. Optical studies show that the transient intermediate produced by photolysis can be observed out to 5 milliseconds. In Figure 2 are the spectra of the unphotolyzed 5-coordinate "base-off" methylcobalamin and the photoproduct using the time resolved flow apparatus for x-ray spectroscopy. The photoproduct spectrum shows a significant decrease in the 1s-3d peak and the appearance of the 1s-4p+SD peak indicating a 4-coordinate species. This work was supported by the NSF grant #BIR-9317769.

Figure 1.

Figure 2.

X-RAY DIFFRACTION OF AMPHIPHILIC LIPIDS AND MODEL SURFACTANTS ON A LANGMUIR SURFACE.

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Pulmonary surfactant is a complex mixture of phospholipids, neutral lipids, glycolipids, and protein at the air-liquid interface of the alveoli. It is composed primarily of phospholipid of which dipalmitoylphosphatidyl choline (DPPC) is the largest constituent. The surfactant monolayer significantly reduces the surface tension at the air-liquid interface at functional residual capacity (FRC), thus reducing the amount of work required to inflate the lungs. Structural information as to the conformation and interaction of the various components of the surfactant monolayer may lead to the development of better replacement compounds, as well as improve our basic understanding of how phospholipids and proteins behave at an air-liquid interface. We report the observation of both meridional (0,0,s_z) and in-plane (s₁,s₂) scatter from a DPPC monolayer spread at a Langmuir surface (z axis ⊥ to the liquid surface). An optical flat was oriented in the experimental hutch to deflect a monochromatic (8.05 keV) x-ray beam and provide control of the grazing angle, ω, of the incident beam with the Langmuir surface. The x-rays were focused vertically at the center of a KSV mini-trough and horizontally at the detector. The specimen to detector distance was either 224mm (in-plane and meridional) or 373mm (meridional) from trough center. The trough was mounted on a vibration isolation table which could be translated vertically to align the sample. The specular reflection of the incident x-ray beam (ω = 3.0 mrad) from the air liquid interface was monitored during the experiment in an effort to track the interception of the x-ray beam with the surface. By monitoring and correcting for changes in the water height of the subphase, we were able to maintain the sample height to within 50 μm. Two-dimensional data was integrated along the meridional axis and background corrected. At surface pressures ranging from 20 - 40mN/m we observed two broad maxima along the meridian corresponding to the structure factor modulus squared of a single monolayer projected onto the z-axis. Similar data was collected using a PSD detector aligned along the meridian, and is shown in figure 1. We obtained acyl-chain data for DPPC at 4, 30, and 45 mN/m by observing the in-plane scatter. A 1-dimensional PSD detector was mounted parallel to s₂ and scanned horizontally in 2θ. Soller slits (angle acceptance=0.75°) were used to improve Δq resolution. For the higher pressures we observed a maxima at 4.1Å and a broad diffuse signal between 4.2Å - 4.6Å. The former is at angle of 34° with respect to the equator, and the later is centered on the equator. No signal was observed at 4 mN/m. This data is consistent with domain formation upon compression, with an ordered domain at 4.1Å and a disordered domain at <4.4Å>. The authors would like to thank the X-ray Scattering Group (X22) for the use of the vibration isolation table.

Figure 1 Meridional intensity as a function of surface pressure

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STRUCTURAL CHARACTERIZATION OF ORGANO-CUPRATE REAGENTS

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Organocopper compounds are among the most versatile organometallic reagents for forming new carbon-carbon bonds. Although the synthetic utility of these reagents is well established, their reaction mechanisms and their structures remain controversial. Several recent crystal structures have shown that both "lower-order" (2-coordinate) and "higher-order" (3-coordinate) organocuprate anions can exist in the solid state. Despite extensive study, the structures of cyano-substituted copper reagents, prepared by the reaction of RLi with CuCN, remain particularly unclear, with significant controversy regarding the existence of "higher-order" cuprates [1,2].

Initial EXAFS studies [3], performed on beam-line X9A demonstrated that the so-called higher-order cyanocuprate reagents do not in fact contain coordinated cyanide (see Figure). This work has now been extended to include alternative sources for the organo group. Solutions prepared using Grignard reagents (BuMgBr) as the alkyl source are structurally identical (from an EXAFS perspective) to the solutions prepared using BuLi. Similar results are obtained using aryl reagents (e.g., phenyl lithium). In all cases, the reagents appear to go from two-coordinate for CuCN(s) to 3-coordinate for the solubilized CuCN·2LiCl and back to 2-coordinate for Cu(CN)R⁻ and CuR₂⁻. Outer shell scattering indicates that there are an average of ca. two coordinated cyanides for 1, one coordinated cyanide for 2, and no detectable cyanide coordination for the so-called "higher-order" cuprate reagent 3. The absence of EXAFS detectable Cu...N scattering could, of course, arise from the presence of bent cyanide ligands (which would have greatly decreased multiple scattering). Such a bridging geometry is extremely rare in Cu(I) cyanides. Moreover, the apparent first shell coordination number, the first shell bond lengths, and the XANES spectra all point to the presence of 2-coordinate Cu(I) in both 2 and 3, thus excluding the possibility that any significant amount of "Bu₂Cu(CN)₂⁻" is present in 3. These results suggest that it is necessary to re-evaluate the prevailing interpretations of organocuprate chemistry.

Fourier transforms of the EXAFS data for CuCN·2LiCl (1), and 1+1 or 2 equivalents of BuLi (2 and 3 respectively). Spectra offset vertically for clarity.

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X-RAY ABSORPTION SPECTROSCOPY OF THE IRON SITE IN *E. COLI* FE(III) SUPEROXIDE DISMUTASE

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Superoxide dismutase (SOD) catalyzes the disproportionation of superoxide to hydrogen peroxide and dioxygen. The iron and manganese forms of several bacterial SODs have been well characterized and shown to be structurally similar. The metal is coordinated to three histidine nitrogens and one aspartate oxygen, with several conserved aromatic residues near the active site. Although the *E. Coli*¹ and *Pseudomonas Ovalis*² FeSODs have the same overall protein folding pattern, their iron site structures appear to be distinct. The *E. Coli* Fe enzyme shows a trigonal bipyramidal iron (the fifth ligand coming from solvent) while the *Ps. Ovalis* structure has a tetrahedral Fe with no evidence for the inclusion of solvent. In addition there are significant variations in metal-ligand distances, with the *E. Coli* and the *Ps. Ovalis* structures having average iron-ligand distances of 2.0 Å and 2.4 Å, respectively.

Small molecules have been shown to act as inhibitors of FeSOD, and small anions such as azide and fluoride produce spectral changes suggestive of an increased coordination number for the iron on anion binding. The crystal structures of the azide derivatives of both the *E. Coli* and *Ps. Ovalis* FeSOD have been determined. Neither structure shows a loss of protein ligands on azide binding and no evidence for loss of the bound solvent from the *E. Coli* enzyme. This leads to proposals for 6- and 5-coordinate sites, respectively.

Ferric SOD shows two pH dependent spectral perturbations in its EPR and UV-Vis spectra, with apparent pKs of 5.1 and 9.0, that are linked to changes in the catalytic activity of the enzyme. K_m is strongly dependent on pH above pH 8 and K_d for azide binding increases above pH 7.5, with an apparent pK of 8.6. The high pH transition is linked to the uptake of one proton, and has been attributed to the deprotonation of a bound water. Alternatively, this transition could be due to binding of exogenous hydroxide ion.

We have used X-ray absorption spectroscopy to determine the local structure of the iron site in ferric superoxide dismutase from *E. Coli*. Azide and high pH both cause a significant reduction in the intensity of the 1s → 3d transition (see Figure). In the resting state of the enzyme, the iron is five coordinate with an average metal-ligand bond length of 1.98 Å, consistent with the Stallings structure. Binding of azide causes an increase of 0.08 Å; Raising the pH from 7.0 to 9.4 leads to a 0.04 Å increase with a further ~0.01 Å increase when the pH is raised to 10.0. The changes in both 1s → 3d area and bond length indicate an increase in the iron coordination number from five to six on anion binding, thus suggesting a molecular mechanism for the pH dependent inhibition kinetics.

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XANES spectra for *E. Coli* SOD. A=ferric pH 7, B=ferric +azide, C=ferric, pH 9.4. Inset: Isolated 1s → 3d transitions for A-C (top to bottom).

X9B

SOLUTION SCATTERING STUDIES OF THE ADHESIVE PROTEINS FROM THE BLUE MUSSEL MYTILUS EDULIS.

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The Blue Mussel (*Mytilus edulis*) is a common intertidal bivalve. In order to maintain its location in this turbulent region, the mussel has evolved an attachment mechanism known as a byssus. Two of the major protein constituents of the byssus are Mefp 1 and 2. We are currently focusing on the solution structure of Mefp 2, a 40kD protein containing large amounts of CYS and DOPA (dihydroxy-phenylalanine). FTIR measurements of Mefp 2 indicate that, in contrast to Mefp 1, the protein contains large amounts of alpha helical secondary structure. Biochemical studies of Mefp 2 indicate that the protein has extensive internal crosslinks and is extremely resistant to proteases. Our previous work at NSLS has shown that Mefp 1 has an open extended structure in solution. Mefp 2 exhibits a solution scattering profile markedly different from that of Mefp 1, presumably due to Mefp 2's extensive secondary structure. Initial data analysis indicates that Mefp2 assumes a spherical conformation in solution and has a radius of gyration of approximately 20Å. There is also evidence for either the irreversible formation of an aggregate or a conformational change in Mefp 2 in the presence of trace amounts of Mefp 1. These experiments are currently being repeated. This work is supported by a NRSA Postdoctoral Fellowship # 1 F32 DE05612-01A1 (Dr. Trumbore).

X9-B

RESOLVING DIFFRACTION FROM THE LARGE UNIT CELL PROTEIN CRYSTALS WITH SAGITTAL FOCUSING

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Macromolecular crystals with large unit cells require small spot sizes of the x-ray beam on the detector at medium to large specimen-detector distances. The diffraction pattern of steroid isomerase, a protein crystal with a 500 Å length of the unit cell in one dimension and about 50 Å in the other two dimensions, could not be well resolved at the crystallography beamline X8C of the Structural Biology Center. The collimator would provide small spot sizes at short distance but at the longer detector distance required aberrations due to the toroidal mirror produced too large spot sizes.

The goal of the experiments is to see if and under which conditions the different focusing optics of beamline X9 can resolve diffraction patterns of large unit cell protein crystals. Beamline X9 uses a sagittally focusing crystal in the double crystal monochromator to focus in the horizontal direction and a cylindrically bent, flat mirror for focusing in the vertical direction. The two focal points are independent of each other. Beamline X8C uses a single bent cylinder (torus) for point-focusing the beam. In all experiments, the crystal of dimension 0.88 mm (in direction of the 500 Å unit cell dimension) by 0.3 mm was mounted with the direction of the 500 Å unit cell approximately parallel to the rotation axis.

For the first experiment, the rotation axis was set vertical so that the dense 500 Å reflections would be in the vertical direction where the focal size is smallest. The beam was focused on the detector in vertical direction. The measured focal height was 0.12 mm FWHM. In horizontal direction, the beam was focused on the crystal for maximum flux. The specimen-to-detector distance was 300 mm. The diffraction pattern recorded with the CCD-detector of beamline X8C and with an image plate showed that the 500 Å reflection were resolved with the intensity reaching about background between reflections.

In the second experiment, the rotation axis was set as is standard for synchrotron because of the horizontal polarization. In this case, the horizontal focus was on the detector - spot size 0.33 mm FWHM - and the vertical focus on the specimen. The diffraction pattern recorded with the image plate, showed some overlap between the 500 Å reflections. It was noted that the FWHM of the reflections was much larger than the measured focal size. The probable explanation is widening of the reflections due to the large horizontal convergence of the focused beam. The effect will be studied in the third experiment.

Beamline X9B is supported by NIH RR-01633

XAS INVESTIGATIONS OF THE H₂-BINDING SITE IN HYDROGENASE.
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Hydrogenases are enzymes that catalyze the reversible oxidation of H₂ in bacteria.¹ All H₂ases contain Fe/S clusters and most contain a Ni center as well. In Ni-containing hydrogenases, the Ni site has been implicated as being involved in the binding of substrate (H₂) and carrying out the associated redox reaction. Recently, an active form of the enzyme (Form C) that has been described as containing a Ni-H or Ni-H₂ complex was shown to be light sensitive.² Exposure to light produces a form of the enzyme that exhibits a unique epr signal. ENDOR experiments revealed that there is a proton with a unique coupling constant (20 MHz) present in the Form C sample that is lost upon irradiation.³ Nickel K-edge XAS in the XANES region (Figure 1) was utilized to look for edge energy differences that might be associated with a change in electron density on the Ni center and to examine pre-edge features for changes associated with a change in coordination number/geometry. EXAFS analysis (Figure 2) was used to detect Ni-S bond length changes that might also occur upon photolysis. Analysis of the XAS data reveals that there is no significant difference between the unexposed and photolyzed samples. This data is incompatible with a strong interaction between the Ni center and H⁺ or H₂ in the enzyme.

Figure 1. Ni K-edge XANES spectra of Form C before (solid line) and after (dashed line) exposure to light.

Figure 2. Unfiltered EXAFS spectra of unexposed (top) and light-exposed (bottom) samples of hydrogenase.

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X-RAY ABSORPTION SPECTROSCOPY OF THE COBALT(I) INTERMEDIATE INVOLVED IN ACETYL COENZYME A SYNTHESIS BY *Clostridium thermoaceticum*

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The corrinoid/iron-sulfur protein (C/Fe-SP) from *Clostridium thermoaceticum* cycles between a methyl-Co(III) and Co(I) form as it transfers a methyl group from methyl-tetrahydrofolate to carbon monoxide dehydrogenase. Extended X-ray Absorption Fine Structure (EXAFS) and x-ray edge spectroscopy of the active Co(I) state of the C/Fe-SP indicates a four-coordinate (distorted) square-planar structure where the best fit gave average Co-N(equatorial) distances of 1.87 ± 0.01 Å, corresponding to 4.2 ± 0.3 ligands. The x-ray edge spectrum of Co(I) C/Fe-SP contains a moderate intensity 1s-4p + shake-down transition and no 1s-3d peak (where shake-down (SD) transitions are indicative of square-planar geometries). X-ray edge results for the methyl-Co(III) form, reported earlier, are consistent with a base-off methylcobamide structure which is five-coordinate at physiological temperatures and six-coordinate, with a water ligand in place of the benzimidazole ligand, at low temperature (Wirt *et al.*, *J. Am. Chem. Soc.* 1993, 115, 2146). The absence of a ligated benzimidazole base in the methyl-Co(III) state is important since the base-off form is expected to predispose the Co-C bond toward heterolytic cleavage to form four-coordinate Co(I). Additionally, we have examined first derivative x-ray edge spectra of Co(I) C/Fe-SP relative to edge spectra of a cobalt foil as an indicator of effective nuclear charge on cobalt. The Co(I) C/Fe-SP edge position at 7720.5 ± 0.3 eV is consistent with previous trends noted in free cobalamins shifting ca. 0.5 eV to lower energy for each one electron reduction from Co(III) to Co(I) C/Fe-SP. Interestingly, edge shifts observed for the C/Fe-SP series are both smaller in magnitude and occur at lower energies than their free cobalamin analogues (see reference cited above). This reduction in effective nuclear charge for protein bound cobalt may be related to the mechanism the enzyme utilizes to facilitate conversion of the methyl-Co(III) C/Fe-SP species to Co(I) in the methyl transfer reaction.

ZINC FINGER IDENTIFICATION IN GIARDIA LAMBLIA BY EXAFS

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Giardia lamblia (*Giardia*) is a parasite of humans and other mammals and the most common disease-causing pathogen worldwide. *Giardia* undergoes surface antigenic variation by variant-specific surface proteins (VSPs). VSPs cover the entire surface of *Giardia*, are rich in cysteines, and bind heavy metals, particularly zinc.

Zinc fingers are a class of proteins that bind nucleic acids and have four amino acids (either cysteines or histidines) directly bound to the central atom--zinc. Since VSPs are cysteine rich with large amounts of zinc, we explored the possibility that *Giardia* has large quantities of zinc and whether the zinc has sulfur coordination.

To determine the quantities of zinc, we performed x-ray microanalysis of *Giardia* whole cell samples on beamline X9B. Characteristic peaks were identified according to the standard atomic emission energies. As shown in a typical energy dispersive spectrum of *Giardia* (Figure #1), the concentrations of elements in *Giardia* with x-ray fluorescent emission energies ≥ 1000 eV were exhibited directly. The results demonstrate relatively large amounts of zinc in *Giardia*.

Subsequently, we collected EXAFS data on the *Giardia* preparation to analyze the ligands around zinc (Table #1). It was a surprise to see the data adequately fit with a zinc sulfide model (average Zn-S distance of 2.352 ± 0.005 Å, and coordination number of 3.72-4.36). However, the best results were obtained with a two atom fit (ZnS and zinc tetraphenyl porphyrin (ZnTPP), 4S/0.5N). Those results are consistent with the bulk of zinc in *Giardia* coordinated to cysteinyl sulfurs in the VSPs while a small but expected fraction of zinc enzymes (typically with histidine and/or water coordination) contributes to the spectrum.

Figure 1

UNKNOWN	MODEL	N	Ratio	χ^2
GIAR DC	ZNS	4	0.003	0.15
GIAR DC	ZNS	4	0.003	0.91
	ZNTPP	1	0.011	6.75
GIAR DC	ZNS	4	0.003	0.72
	ZNTPP	0.5	0.003	5.11

Table 1

PROFILE AND IN-PLANE STRUCTURES OF SELF-ASSEMBLED MONOLAYERS ON GE/SI MULTILAYER SUBSTRATES BY HIGH-RESOLUTION X-RAY DIFFRACTION EMPLOYING X-RAY INTERFEROMETRY/HOLOGRAPHY

S. Xu (U. of Pennsylvania), R. F. Fischetti (Biostructures Inst.), J. K. Blasie (U. of Pennsylvania), L. J. Peticolas (AT&T), and J. C. Bean (AT&T)

X-ray interferometry has been used to study the profile structures of chemisorbed alkylsiloxane (hexadecyl-, octadecyl- and eicosyl-) monolayer films on Ge/Si multilayer substrates of the type $2(\text{Ge}_2\text{Si}_{30})$, i.e., two superlattice unit cells, each consisting of two Ge monolayers and thirty Si monolayers, as fabricated by molecular beam epitaxy (MBE). Analysis was performed in three steps. First, based on the structural specifications of the cleaned, bare substrates acquired from the MBE fabrication, the actual profile structures of selected multilayer substrates were determined via a model refinement analysis of their meridional x-ray diffraction. The partial profile structures of these substrates (e.g., $\text{Ge}_2\text{Si}_{30}\text{Ge}_2$) were then employed as the reference profile structure to perform a highly constrained, real-space refinement analysis to derive the profile structures of these multilayer substrates including the particular self-assembled monolayers on their surface, as relative electron density profiles from their meridional x-ray diffraction. Lastly, a real-space refinement was applied to convert the relative electron density profiles to their equivalent profile structures in absolute electron density. These profile structures demonstrate the alkyl chain configurations in these self-assembled monolayers are all-trans and tilted, with respect to the surface normal. The tilt angles are approximately $32 \pm 3^\circ$, $31 \pm 3^\circ$, and $30 \pm 3^\circ$ for the 16C, 18C, and 20C chains, respectively. The terminal methyl endgroups of each monolayer seem to be well ordered in the profile structure, all lying in the same surface plane to within ± 1 Å. We also discovered that a layer of SiO_x between 15 Å and 18 Å thick was formed at the surface of the substrates during our pre-alkylation cleaning procedures. The profile structures so-derived via x-ray interferometry were further proven to be correct by inspection of the Patterson function, derived uniquely from the meridional diffraction without phase information, by analogy to off-axis Fourier holography. This overall approach, which does not require either the determination of explicit phase information or the pre-assumption of any model parameters, is therefore very powerful for uniquely determining the unknown profile structure of the organic overlayer including the substrate/overlayer interface. The in-plane structures of the 16C and 20C self-assembled monolayers were also investigated by high-resolution x-ray diffraction. In both cases, the in-plane structure was found to be distorted hexagonal ($b/a \approx 2.08$, Area/chain ≈ 17 - 19 Å^2 , correlation length $\approx 260 \text{ Å}$) with a nearest neighbor chain tilt direction.

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X-RAY DIFFRACTION BASED STRUCTURAL STUDIES OF THE ACETYLCHOLINE RECEPTOR MEMBRANES FROM *T. CALIFORNICA* AND *T. NOBLIANA*
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The nicotinic acetylcholine receptor (AChR) is a neurochemically-gated cation-selective channel found in the neuromuscular junctions of vertebrates and the electrogenic organs of marine elasmobranchs and teleosts. The release of neurotransmitter from the nerve terminus induces a transient increase in cation permeability and subsequent depolarization of the postsynaptic membrane. The AChR is perhaps the best characterized integral membrane neurotransmitter receptor and has been the focus of intense structural studies, owing to the existence of appropriate biological sources and its natural abundance in the plasma membrane. This receptor is a large molecular weight (~295kDa), oligomeric ($\alpha\beta\gamma\delta$ hetero-pentamer), integral membrane protein whose three-dimensional shape has been determined by electron microscopy and low-resolution x-ray diffraction. Elements of secondary structure of the AChR have begun to be identified through cryoelectron microscopy of tubular crystals (Unwin, 1993). In the absence of a crystal structure, an x-ray diffraction based structural analysis of the native AChR membrane is underway in our laboratory. AChR-containing membranes from *T. californica* and *T. nobiliana* have been purified to near homogeneity ($\geq 65\%$ and $\geq 80\%$ AChR, respectively, by weight protein). Fully oriented stacks of AChR membranes for x-ray diffraction have been prepared and these samples give reproducible x-ray diffraction patterns indicative of a lattice organization parallel to the sedimentation axis, and a hexagonal lattice organization of the receptor molecules in the plane of the membrane. Analysis of the meridional diffraction pattern revealed an approximately 450Å lattice spacing between stacked vesicle membrane pairs with a resolution of approximately 10Å. Due to the large unit cell size and the weak nature of the membrane diffraction from this system, the low angle diffraction data has been collected at NSLS, beamline X9 and correlated with the higher angle diffraction data collected in our laboratory. In the plane of the membrane (perpendicular to the sedimentation axis), the AChR molecules are organized in a hexagonal lattice with a lattice constant of approximately 82Å (center-to-center spacing between adjacent AChR molecules). At higher angle, the in-plane structure gave rise to diffraction characteristic of α -helix and acyl-chain packing.

A structure has been determined for the AChR membrane multilayers to 15Å (Figure 1) using the recursion method of Hosemann and Bagchi (1962). Interpretation of the electron density profile has been inferred to be the following: the cytoplasmic (protein) extension is 28Å, followed by a bilayer thickness of 57Å (42Å headgroup to headgroup spacing) and a synaptic (protein) extension of 84Å for a molecular length of 169Å. This interpretation is consistent with radial density distributions of the AChR membranes as determined by cryoelectron microscopy of tubular crystals (Toyoshima and Unwin, 1990; Unwin, 1993). Experiments are underway at NSLS, beamline X9 to verify these assignments using halogenated-agonists of the AChR as probes for the locations of the acetylcholine binding sites. Determining the locations of the halogen atoms will allow us to confidently delineate the AChR structure within the electron density profile, and allow us to verify our phase assignments. [Supported by Miles Pharmaceuticals Division, Miles Inc., A Univ. of Conn. Health Ctr. Grant, NIH 2P01H118608 and NIH RR01633]

Figure 1 Electron density profile for half the unit cell with the synaptic extension on the right.

CARBOXYPEPTIDASE AND ITS INTERMEDIATES

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Systematic X-ray Absorption Fine Structure (XAFS) experiments have been performed to probe detailed structural changes in the metal environment of the metalloprotease, carboxypeptidase-A (ZnCPD) in its solution form as a function of pH. The XAFS spectra of ZnCPD show progressive spectral changes particularly in the near edge region when the pH is changed from neutral to alkaline values. Data analysis yield two distributions of atoms in the first coordination shell of ZnCPD at all pH values at both 150 K and 297 K. Direct comparison of the first and higher coordination shells of ZnCPD reveals structural differences between pH 7 and 10 which is principally reflected in the average inner coordination distance decreasing 0.022 Å as the pH is increased. The XAFS Debye-Waller factor shows an increased structural disorder for the 4 atom distribution at the alkaline pH values. However, the higher shell comparison shows that the histidine ligands remain unchanged at the pH values examined. The observed structural changes indicate one of the ligands to the metal moves 0.09 ± 0.03 Å closer to the zinc ion at alkaline pH values, resulting in shorter average metal-ligand distance and an increased first shell structural disorder. The plot of the normalized spectral changes at the absorption edge as a function of pH conforms to a theoretical pH-titration curve with a pK_a of 9.49 at -4° C, the freezing point of the 1 M NaCl cryosolvent. This value corresponds to that obtained by extrapolation of the temperature dependent value of pK_{EH} obtained by kinetic analysis of the carboxypeptidase-A catalyzed hydrolysis of tripeptides. The structural changes can be attributed to the ionization of the water coordinated to the catalytic zinc ion. This ionization strengthens the Zn-OH bond, and prevents displacement of hydroxide by substrates and inhibitors. Thus, it is likely that ionization of the ligated water molecule in ZnCPD is responsible for the diminished activity at alkaline pH values. Future studies will determine whether or not the XAFS determined pK_a is responsive to inhibitor binding as is the kinetically determined pK_{EH} .

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X9-A

Polarized XAFS Studies on Myoglobin Single Crystals

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Polarized XAFS experiments have been performed on a Met-myoglobin single crystal sample. The single crystal was sealed in a glass capillary with mother liquor of pH 7 to maintain the humidity of the sample. The desired orientations of the crystalline sample relative to the X-ray polarization were obtained using a Huber 4-circle goniometer. The measurements were performed under fully focused operation of Beamline X9-B to issue sufficient photon flux on the protein crystal, which has a dimension of $0.3 \times 1.0 \times 2.0 \text{ mm}^3$.

Figure 1 shows the XAFS χ function with the X-ray polarization parallel (solid) and perpendicular (dash) to the heme plane. Substantial spectral differences are found at the two extreme crystal orientations. Detailed XAFS data analysis shows that the iron ligands in the heme plane are located at an average distance of $2.03 \pm 0.01 \text{ \AA}$ from the metal ion, while the axial ligands are located at an average distance of $2.12 \pm 0.02 \text{ \AA}$. Using polarized XAFS we will be able to determine the structure of the iron site of myoglobin in a much greater detail.

Figure 1. XAFS χ data of met-myoglobin with the X-ray polarization parallel (solid) and perpendicular (dash) to the heme-plane.

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Reflectivity Studies of the Langmuir-Blodgett film Melting X10A,B

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The temperature dependence of Langmuir-Blodgett (LB) film structures, particularly structural changes as the LB film is melted, is of interest to both science and potentially industrial applications. We have prepared multilayers of cadmium arachidate on silicon substrates and studied the structure changes as a function of temperature via the X-ray reflectivity technique at the Exxon beam line X10B. The figure shows the X-ray reflectivities at 60, 100, 108, 117 and 121°C of a 9 layer film, displaced 2 decades apart for clarity. At higher temperatures, the positions of the Bragg peaks shift slightly to larger q values, indicating thermal expansion of the layer thickness. More significantly, the main peak intensities, which corresponds to the interlayer order, diminish continuously for increasing temperature. The amplitude of the side peaks, which arise from the total layer thickness, do not vary until the final melting when temperature is between 117°C and 121°C. The detailed analysis of these reflectivities and future grazing incident diffraction studies of the inplane order should reveal more complete details of the LB film melting process.

DISSOLUTION AT THE CALCITE-WATER INTERFACE

R. P. Chiarello, N. C. Sturchio, and R. A. Wogelius (ANL)

Reactions occurring at mineral-fluid interfaces play a crucial role in geochemical transport processes. The fundamental atomic-scale reactions of mineral dissolution and growth occur at mineral-fluid interfaces. We have demonstrated the applicability of synchrotron x-ray reflectivity (XR) to in-situ study of mineral-fluid interfaces by a preliminary experiment with calcite (CaCO_3). Shown in figure 1 is XR data recorded for a pristine calcite (1014) cleavage surface in contact with dry N_2 gas, and for the same surface in successive contact with humid N_2 , deionized water (DIW, pH = 5.60), and dilute nitric acid solutions having initial pH values of 4.20, 3.26, and 2.31. The roughness of the pristine calcite surface in contact with dry N_2 was 2.6 Å, which is comparable to the Ca-O bond distance in calcite. The width of the calcite/fluid interface was 23.1 Å following reaction with DIW and this width increased to 45.3 Å following reaction with dilute nitric acid solutions.

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Figure 2 shows an interpretation of these XR results in terms of the calcite/fluid interfacial width. For dissolution at pH values of 5.60 and 4.20 the XR results are consistent with angstrom-scale roughening of intraterrace areas. At pH values 3.26 and 2.31, a model including both the formation of μm -size etch pits and Å-scale roughening of intraterrace areas was consistent with these XR results and other observations made by atomic force microscope and other microscopic imaging techniques.

Anomalous X-Ray Reflectivity Studies Of Electrochemically Induced Roughness And Pit Formation On Metal Surfaces

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A quantitative description of the development of surface roughness in metals and alloys is of great importance in a number of fields, e.g. catalysis, corrosion, etc. This particular study was aimed to elucidate the process of electrochemically induced corrosion and pit formation at the solution/Cu oxide and Cu oxide/Cu interfaces via x-ray scattering techniques.

Both specular reflectivity and diffuse scattering were measured on thin (~ 1500 Å) Cu films evaporated on single crystal Si(111) substrate. Measurements were carried out in an x-ray/electrochemical cell in various solution environments and as a function of the applied electrical potential. The specular reflectivity was taken at three different photon energies near the Cu K absorption edge (8979 eV). Typical results are shown in Fig. 1. Changes in both the specular reflectivity and the diffuse scattering were observed as the applied potential was varied from the negative (cathodic) region (-0.90 V vs. SCE) where the Cu surface is relatively free of oxide film to the positive (anodic) region ($+0.25$ V) where surface roughening occurs by general corrosion with concomitant formation of copper oxide films. Changes have also been observed in the potential region of $+0.4$ to $+0.65$ V where localized corrosion or pitting occurs.

Quantitative analysis of the experimental results is in progress. We hope to obtain a direct correlation between the pit size and the applied potential. We also hope to extend these studies to single crystal surfaces and to other metals like iron and/or nickel.

CHAIN-LENGTH DEPENDENCE OF THE STRUCTURES AND PHASES OF $\text{CH}_3(\text{CH}_2)_n\text{-SH}$ SELF-ASSEMBLED ON $\text{Au}(111)$

X10A,B

P. Fenter, N. Camillone III, J. Li, G.-Y. Liu, G. Scoles, and P. Eisenberger (Princeton U.), C. E. D. Chidsey (Stanford U.), and K. S. Liang (Exxon)

We have performed a comprehensive grazing incidence x-ray diffraction study of the structures and phases of $\text{CH}_3(\text{CH}_2)_n\text{-SH}$ ($10 \leq n \leq 30$) self-assembled on a $\text{Au}(111)$ surface [1,2]. From measurements of the 'as-deposited' and annealed states (Figure 1) of these self-assembled monolayers (SAM's), we show that the SAM, when prepared under typical conditions, has only a limited domain size, typically $\sim 100 \text{ \AA}$. We also find that the self-assembly process results in a non-equilibrium state with a specific defect structure, which is characterized by a modulation of the monolayer diffraction peak positions [1]. We have also performed a careful comparison of results from both x-ray and He atom diffraction [2], which have very different sensitivities to presence of defects. These results show differences in the measured linewidths, which we find is a consequence of the effective domain wall width as seen by the two techniques. These results suggest a model of the self-assembly process at room temperature which involves chemisorption followed by a kinetically limited and chain length dependent reorganization process.

We have also explored the global (n,T) phase diagram[1]. Measurements of the rod structure of the monolayer diffraction reveal that the tilt structure exhibits distinct 'long' ($n \geq 16$) and 'short' ($n \leq 14$) chain length regimes. In addition, there are striking differences in the high temperature phase behavior. While for $n \leq 12$ the monolayer melts from the hexagonal phase, for $n \geq 14$ we find that the monolayer exhibits a commensurate-incommensurate transition. These results demonstrate that SAM's exhibit a more complex phase behavior than was previously believed. We are currently extending these studies to directly study the self-assembly process.

[1] P. Fenter, P. Eisenberger, and K. S. Liang, Phys. Rev. Lett. 70, 2447(1993).

[2] N. Camillone III, C. E. D. Chidsey, P. Eisenberger, P. Fenter, J. Li, K. S. Liang, G.-Y. Liu, and G. Scoles, J. Chem. Phys. 99, 744(1993).

Multistage Faceting of $\text{Pt}(11\text{n})$ Surface

X10A,B

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A sequence of faceting transitions is identified on a Pt surface oriented to the $\langle 115 \rangle$ direction by surface X-ray scattering measurements. The directions of the crystal truncation rods (CTR's) from the bulk Pt (002) Bragg peaks as a function of temperature are illustrated in the Figure by plotting the angles between the CTR's and the normal direction of the sample surface, *i.e.*, the $\langle 115 \rangle$ direction. Below 600 °C, the surface phase separates into the (117) facets and rough regions. At higher temperatures, the (117) facets are replaced by the (119) facets (at 650 °C) and subsequently by the (1 1 13) facets (at 700 °C). All the observed facets are macroscopic in size ($> 1000 \text{ \AA}$), deduced from the sharpness of the CTR's. The surface only becomes (115) at much higher temperatures, above 1000 °C, indicating that the (115) does not belong to the ECS at low temperatures. A 3-fold surface reconstruction (in region (e)), and a 5-fold surface reconstruction (in region (d)) are also found. The existence of these surface reconstructions on the (117) and the (119) facets strongly suggests that the faceting transitions are driven by the reconstruction transitions. The limited terrace sizes of high-index facets alter the nature of the reconstruction transition and induce the faceting transition. At low temperatures, the reconstruction on the (117) facet makes the surface phase-separate into the (117) facets and round area to minimize the surface free energy. At temperature above 600 °C, the (117) reconstruction ceases to exist and the next available channel in reducing the free energy is the 5-fold reconstruction on the (119) facets. This reconstruction is then also destroyed by raising temperature above 700 °C and the (1 1 13) facets dominant. Above 1000 °C, no reconstruction on this surface exists anymore, and surface become (115).

The direction of the CTR as a function of temperature.

The Counterion Overlayers at the Electrolyte/Self-Assembled Monolayer Interface

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Self-assembled monolayers (SAM's) of long chain alkane thiols on Au single crystal surface is one of the most well characterized ordered organic films. Following our previous studies in the UHV environment [1,2], we have recently investigated the electric double layers formed at the electrolyte-SAM interface using x-ray reflectivity measurements. By modifying the top methyl group of the SAM to carboxylic group, we were able to determine the formation of the counterions overlayers from the density profile. So far, different counterions of Hg^+ , Cd^{++} , and Pb^{++} have been studied under electrolytes with different ion concentrations and pH values. The figure (a) illustrates the case when the electrolyte was 0.5 mM HgNO_3 at $\text{pH}=3.95$. From the strong oscillation observed in the reflectivity curves, the electron density profiles can be obtained by curve fitting, shown in figure (b). In the case shown, the Hg ion density per unit area turns out to be about one Hg^+ per carboxylic head group of the SAM surface. By systematically mapping out the counterion density profiles for different electrolytes by varying ion concentration and pH values, we should be able to reveal the nature of the electric double layers in the SAM systems, which would have implications in such area of interest as biomineralization.

1. P. Fenter, P. Eisenberger, and K. S. Liang, Phys. Rev. Lett. **70**, 2447 (1993).
2. N. Camillone III, et al., J. Chem. Phys. **99**, 744 (1993).

Thermal Roughening of Si (331) Surface

x10A,B

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We have identified that the (331) surface of silicon is a stable facet at low temperatures that undergoes a thermal roughening transition at 810°C. Sharp specular reflection and crystal truncation rods below 800°C indicate the existence of large clean (331) facets. Above 800°C, the sharp specular and non-specular reflections are replaced by the diffuse scattering from a rough surface. The nature of the transition was revealed by studying the detailed scattering profile near the transition.

The bulk of data is taken at the specular rod with q_z (the momentum transfer perpendicular to the surface) fixed at 0.5 r.l.u., where the diffuse scattering from the rough surface can be measured easily. As illustrated in Figure 1, the sharp component from the flat (331) facets disappear progressively across the transition. The transition was completely reversible and reproducible. Near the transition, the diffuse scattering very close the peak is rather suppressed. This may be interpreted as an evidence for the coexistence of the flat facets and rough regions, in which case the transition is discontinuous first order transition. Our data also suggest that there is a sharp corner in the equilibrium crystal shape of silicon near the $\langle 331 \rangle$ direction. Further analysis will follow to clarify the nature of the transition.

Figure 1. Transverse Scans at fixed $q_z = 0.5$ r.l.u. across the roughening transition temperature

X10A,B

Thickness Modified Phase Behavior in the Normal Alkane Thin Films Studied by Synchrotron X-ray Scattering

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Normal alkanes are important systems; they are one of the most basic organic series and form building blocks for surfactants, lipids and liquid crystals¹. We report here recent x-ray scattering studies of variable thickness films of tricosane (C₂₃H₄₈). The films are obtained by evaporating dilute solutions on clean Si wafers. The experiment was carried out at NSLS on beamline X10B. The phase behavior of these thin films differs from that of bulk normal alkane. The melting temperature is strongly depressed ($\Delta T \sim 10\text{K}$) for the film thicknesses $< \sim 1000\text{\AA}$. Rescaling of the rotator phases is less pronounced, resulting in an altered phase diagram in these thin films. Furthermore, there are indications of a restaking transition from ABC to ABA within the RII phase.

¹ E.B. Sirota, H.E. King, Jr., D.M. Singer and H.H. Shao, J. Chem. Phys., **98** (7), 5809-5824 (1993).

X10A,B

Structural Effects of High Pressure Gas on the Rotator Phases of Normal Alkanes

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The effects of high pressure gases ($P \leq 500$ bar) on the RII, RI and RV rotator phases of 21, 23 and 25 carbon normal alkanes, $\text{CH}_3-(\text{CH}_2)_{n-2}-\text{CH}_3$ were studied via high resolution synchrotron x-ray scattering. We have measured the pressure and temperature dependence of the rotator structures and converted these results to the essential structural parameters: layer spacing, area per molecule, lattice distortion and tilt.¹ The pressure was generated by one of three gases: helium, nitrogen, or argon. In the rotator phases, argon and nitrogen intercalate between the layers while helium acts mostly as a non-interacting pressurizing medium. The thermal expansion and compressibility are anomalously large in the rotator phases is almost totally dominated by enharmonic effects.

The figure shows the area/molecules and the distortion away from hexagonal, of the orthorhombic structure of C₂₁ in the R1 phase.

¹E.B. Sirota, H.E. King, Jr., D.M. Singer and H.H. Shao, J. Chem. Phys., **98**, 5809 (1993)

H₂O₂ REDUCTION ON THE Au(001) SURFACE IN ALKALINE ELECTROLYTE: THE ROLE OF SURFACE STRUCTURE.

Ian M. Tidswell, Nenad M. Marković, and Phil N. Ross (Lawrence Berkeley Laboratory).

Although it has been well known for many years that the Au(001) surface is an excellent catalyst for the reduction of O₂ and H₂O₂, the reason for the enhanced activity is unclear. The figure shows that the Au(001) surface is approximately 10⁴ times more active than the Au(111) surface near -0.2 V for the reduction of H₂O₂ in alkaline electrolyte, and that this activity is largely lost on sweeping the potential to -0.4 V. While it seems clear that the different geometry of the two surfaces is a key component, the reason for the loss of activity near -0.4 V is unclear. Two hypotheses have been advanced: That as the potential sweeps more negative the surface reconstructs to a hexagonal structure similar to the Au(111) surface; or that hydroxyl anions adsorbed on the open (001) structure are consumed in the reduction wave.

We have used in situ x-ray scattering at the (0 0 2.3) position on the specular crystal truncation rod to probe the structure of the surface as the potential is swept through the reduction wave. Using information about the correlation between the x-ray scattering intensity and the fraction of the surface reconstructed [1], we can determine the role of the reconstruction formation on the reduction wave. Using this method, we find that the reconstruction forms with a time constant which is much larger than the time constant at which the catalytic activity is lost. This indicates that the reconstruction formation is *not* the prime factor in the different activity at -0.2 and -0.4 V. Rather the explanation for the high Au(001) activity is the enhanced adsorption of hydroxyl anions on the open (001) structure, as compared to

the Au(111) surface.

[1] I. M. Tidswell, N. M. Marković, C. A. Lucas, and P. N. Ross, *Phys. Rev B*, **47** 16542 (1993)

Top: Reduction and oxidation of 10⁻² M H₂O₂ in 0.1 M KOH solution in a hanging meniscus rotating disk geometry. Bottom: Normalized x-ray scattering intensity at the (0 0 2.3) position on cycling the potential. The right hand scale gives the approximate fraction of the surface reconstructed, as deduced from the x-ray scattering intensity using Ref. [1].

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POTENTIAL DEPENDENT RECONSTRUCTION OF THE Au(011) SURFACE IN ALKALINE ELECTROLYTE.

Ian M. Tidswell, Nenad M. Marković, and Phil N. Ross (Lawrence Berkeley Laboratory).

It is well known that the Au(011)/vacuum interface is reconstructed with a (1×2) "missing row" reconstruction [1]. In sulfuric acid the reconstruction was found to have a (1×3) structure, while in perchloric acid the structure was approximately intermediate between the vacuum and sulfuric acid structures [2]. We have used x-ray scattering to probe the structure of the reconstruction in alkaline (0.1 M KOH) electrolyte and to study the dynamics of the transition between the reconstructed and (1×1) structures.

The location of the reconstruction peaks at $H = 1/3$ and $5/3$ [Fig. (a)] is unambiguous evidence that the reconstruction has a (1×3) structure (the other peaks are due to scattering from bulk gold features, the electrolyte or thin polymer film). The scattering intensity at a point along the (0,0, L) rod is used to determine the potentials at which the reconstruction is formed and removed [Fig. (c)]. The reconstruction was found to form gradually over a wide potential region. Removal of the reconstruction is also a gradual process which occurs somewhat negative of oxide formation (which begins at 0.25 V). From stepping studies it was determined that the reconstruction formed quite rapidly, with a time constant of less than five seconds, but that the lifting at potentials just below 0 V was considerably slower, with time constants of around 10 - 50 seconds.

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Figure (a) shows the in-plane scattering along the (H 0.1 0.1) direction at -0.9 V (squares) and 0.0 V (line) in 0.1 M KOH electrolyte. The arrows show the location of the reconstruction peaks at $H = 1/3$ and $5/3$. Figure (b) shows the cyclic voltammetry for the surface, and Fig. (c) shows the changes in x-ray scattering intensity which occur at the (0 0 1.8) position along the specular rod.

X10A,B

POTENTIAL DEPENDENT RELAXATION OF THE Pt(001) SURFACE IN ALKALINE AND ACIDIC ELECTROLYTES.

Ian M. Tidswell, Nenad M. Marković, and Phil N. Ross (Lawrence Berkeley Laboratory).

The structure of the Pt(001) crystal face in contact with several electrolytes as a function of the crystal potential has been studied. From in-plane surface x-ray scattering and crystal truncation rod (CTR) measurements it was determined that the Pt(001) surface is not reconstructed at any potential, in contrast to the surface in vacuum (which has a hexagonal reconstruction) and to the Au(001) crystal face (which has a hexagonal reconstruction in vacuum and at certain potentials in electrolyte). It was found, however, that the x-ray scattering intensity at positions along the specular and non-specular CTR is a function of potential in the region where a monolayer or more of H is adsorbed on the surface (see figure).

The increase (decrease) in scattering intensity at CTR positions below (above) the Bragg peaks on both specular and non-specular CTR's near 0 V (versus rHe) are indicative of an expansion of the Pt top layer along the surface normal direction near 0 V. Detailed modeling of the (0 0 L) and (1 1 L) CTR's was used to determine the magnitude of the top layer expansion. In 0.1 N KOH electrolyte the top layer spacing was increased by up to approximately 2.5% of a lattice spacing at the most negative potentials, as compared to the lattice at 0.4 V (no H adsorption). In 0.01 N HCl solution the maximum expansion was up to approximately 1.5% of a lattice spacing. In 0.1 N HClO₄ and H₂SO₄ solutions the comparable expansion was up to approximately 1.0% of a lattice spacing. The maximum Pt top layer expansion in the different electrolytes appears to be a function of the maximum H coverage prior to H₂ evolution.

This work was supported by the Office of Basic Energy Science in the Materials Sciences Division of the U.S. D.O.E. under contract number DE-AC03-76SF00098.

Fig. (a) Integrated charge calculated from potential/current sweep data. The dotted line indicates the potential for approximately monolayer H coverage. The solid (dashed) lines were measured on the negative (positive) sweep. Fig. (b) Normalized x-ray scattering intensity changes as a function of potential at the (0 0 1.7) and (0 0 2.3) positions. Figure (c) shows similar data at the (1 1 2.7) and (1 1 3.3) positions.

X10A,B

An X-Ray Scattering Characterization of Kinetics of Acid-Catalyzed Sol-Gel Transitions

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In sol-gel transitions, various physical and chemical processes interact¹ to generate a network macrostructure (the gel) from an undifferentiated matrix (the sol). Starting with tetraethoxysilane (TEOS) in an acidic solution, TEOS first hydrolyzes to form Si(OH)₄; then, at small length scales, individual Si(OH)₄ monomers condense onto each other to form complex structures; at larger length scales these separate structures aggregate fractally², and eventually form the macroscopic network of the gel. While there is widespread agreement on the aggregation process (which results in fractal objects of dimension around 2), the currently accepted view that the Si(OH)₄ monomers polymerize into linear "strands" is not confirmed by our observations. What our data seem to indicate instead is that the monomers condense into objects of size ~10 Å. These "building blocks" provide the material for the subsequent fractal aggregation process.

X-ray scattering measurements probed the time evolution of the aggregates from condensation of the monomers to gelation. The silicon in the TEOS molecule provides the necessary X-ray contrast. The scattering curves differ in the $q < 0.4 \text{ Å}^{-1}$ region, showing the growth of the fractal aggregates with time. Past 0.4 Å^{-1} , the curves fall very nearly on top of each other, indicating that the microscopic structure of the aggregates remains constant throughout the process. The broad feature around 1.8 Å^{-1} is related to the internal structure of the building blocks, which appears to be that of amorphous SiO₂. Both this broad peak and the general shape of the curves are consistent with the picture of monomer condensation into small "blocks" presented above. This interpretation is also supported by Raman scattering experiments, which were carried out separately.

¹ See, for example, C.J. Brinker, K.D. Keefer, D.W. Shaefer and C.S. Ashley, *J. Non-Cryst. Solids* **48**, 47 (1982).

² D.W. Shaefer, J.E. Martin, P. Wiltzius and D.S. Cannell, *Phys. Rev. Lett.* **52**, 2371 (1984).

Figure 1. Scattered intensity for the system H₂O:Ethanol:TEOS 8:4:1, at five different aging times. The point in each curve where the plateau at low q rolls off into a power-law slope is related to the size of the fractal aggregate.

Figure 2. Scattered intensity for the system 16:4:1, at five different aging times. In both 8:4:1 and 16:4:1 one can observe the peak at $\sim 1.8 \text{ Å}^{-1}$, which does not change with time. Background scattering from the solution has been subtracted in all curves.

Oxidation-Reduction Induced Roughening of Platinum (111) Surface*

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We carried out an *in situ* investigation of the electrochemical oxidation of platinum in perchloric acid solutions. The experimental details are given in Ref. [1,2]. The Pt(111) surface roughened by oxidation-reduction cycling typically exhibited no in-plane long range order, and the surface roughness involved only the top layer. The repeated cycles of oxidation-reduction can be considered as an interface growth problem [3]. According to the scaling law of interface growth, the interface width should increase as a function of t^β ; in our situation, time can be replaced by the number of oxidation-reduction cycles.

Assuming a Gaussian distribution symmetric about the original top layer (due to the mass conserving process of the roughening [2]) the surface scattering intensity can be expressed as

$$I_S(\vec{Q}_\perp) \Big|_{\vec{Q}_\parallel = \vec{Q}_\parallel} = \frac{1}{C} \sum_n e^{i(nQ_\perp c + \vec{Q}_\parallel \cdot \vec{r}_{n\parallel}) - n^2/2\sigma^2} \quad (1)$$

where C is a normalization constant and n denotes height of the layer. The width of the interface (σ) may have an intrinsic component (σ_0) due to sample preparation. Therefore, σ has two components: σ_0 and the cycle-dependent width, $W(t)$.

The scaling law [3] can be rewritten as $W^2(t) \sim t^{2\beta}$ in the limiting case of $t^\beta \ll r^\lambda$, and the width can be expressed for an interface growing with a rate of a as,

$$\sigma^2 = \sigma_0^2 + at^{2\beta} \quad (2)$$

We obtained the interface widths as a function of the number of oxidation-reduction cycles and the exponent β from fits to (1 0 L) and (0 0 L) rods of the platinum (in a hexagonal unit) by using Eqs. (1,2) (See Fig. 1). The β values are 0.39(2) and 0.38(1), respectively. Simulation using a random model [1] resulted in $\beta = 0.50$. For comparison, we also show a predicted value of $\beta = 0.25$ based on a 2+1 dimensional growth model such as the restricted solid-on-solid model [4], although a direct relation of our measurements to the computer simulations in 2+1 dimensions is not quite clear.

FIG. 1. The width of the roughened interface vs. number of oxidation-reduction cycles.

We suggest that the dynamic scaling behavior proposed for interface growth models is applicable to cyclic oxidation-reduction roughening of a platinum (111) single crystal surface. Since a typical experimental study in interfacial electrochemistry involves cyclic voltammetry, *in situ* structural studies such as this study and theoretical studies performed in parallel with electrochemical measurements are essential to the development of a deeper understanding of electrochemical interfaces.

* This work was supported by DOE under contract W-31-109-ENG-38.

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Density Measurements of Ultrathin Polymer Films by X-Ray Scattering

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There has been some indication that polymer films of thickness much less than the bulk radius of gyration can have densities different from those found in the bulk (G. Reiter, 1992 MRS meeting, Boston), presumably due to packing differences. In order to determine the film density we prepared thin films of polystyrene(PS), polydimethylsiloxane(PDMS) and polyethylenepropylene(PEP) deposited on polished Si wafers. The oxide on the substrates was removed by HF etching prior to film deposition to provide a surface which was sufficiently attractive to the polymers to insure that all the layers wet the surface. That the layers were smooth and showed no island structures characteristic of dewetting was confirmed independently by Atomic Force Microscopy. The measurements were made with the samples in the liquid state so that the polymer conformations could equilibrate. PEP and PDMS spectra were taken at room temperature while PS spectra were taken at 120°C and 170°C, well above the bulk glass transition temperature of 100°C. Specular scattering spectra for films ranging from 26 Å to 200 Å were recorded up to perpendicular momentum transfer $q_z = 0.55 \text{ Å}^{-1}$ which gave reflectivities $\sim 10^{-8}$. Specular scattering calculations were used to find the polymer layer density as a function of film thickness. A typical spectra is shown in fig.1 and the results are summarized in Fig. 2. Within experimental error, about 5%, the densities of the thin films were found to be equal to the corresponding bulk values.

Figure 1 Specular spectrum (o) and fit (—) of a PDMS thin layer on stripped silicon.

Figure 2 Polymer density as function of film thickness.

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X10A,B

X-RAY SCATTERING STUDY OF SURFACE FLUCTUATIONS OF THIN LIQUID POLYDIMETHYLSILOXANE(PDMS) FILMS

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We have measured the x-ray specular and diffuse scattering from thin PDMS films deposited on polished Si substrates for film thicknesses ranging from 17 Å to 506 Å. The films of thickness 506 Å have diffuse scattering characteristic of surfaces of bulk samples but progressively thinner samples show a gradual transition of the diffuse scattering to spectra similar to that of the solid Si substrate (see fig. 1). In contrast, spectra for a small molecule liquid film, cyclohexane on Si in the range 22 Å to 128 Å (Tidswell et al, *phys. Rev. Lett.* **66**, 2108(1991)), showed that the liquid-like behavior of the surface fluctuations persisted down to the thinnest film studied. We believe the different behavior of the polymers is due to the extended size of the long chain molecules. The bulk radius of gyration of the PDMS used in this study was about 240 Å. For layers with dimensions less than this value significant bridging of polymers from the substrate interface to the free surface must be present. This implies that surface fluctuations will involve stretching of polymer molecules and the resulting elastic free energy cost (see Fredrickson et. at, *Macromolecules* **25**, 2082 (1982)) will modify the surface structure factor $S(q)$. Currently, calculations are being made to include these effects in the computation of the diffuse scattering spectra.

Figure 1. Diffuse scattering at $q_z = 0.20 \text{ \AA}^{-1}$ of PDMS thin films.

X10C

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The synthesis of noble metal colloids has been studied extensively because of their applicability as catalysts in both heterogeneous and homogeneous processes. We have recently reported a general method for the production of metal colloids of elements of Groups 6-11 in organic solvents, thus allowing the utilization of the metal colloids in nonaqueous solvents, a more useful medium with respect to organic reactions. The metal salts are suspended in THF and treated with tetraalkylammonium hydrotriorganoborates to yield metal colloid solutions.

By using two different metal halides simultaneously as the metal precursors coreduction occurs to give a bimetallic product. Bimetallic alloys are of interest because as hydrogenation catalysts they are often highly selective and function at lower temperatures and pressures.

To confirm whether the resulting colloid is a bimetallic alloy or a mixture of the two individual metals, the environment about the metals in a series of Rh_xPt_y and Pd_xCu_y colloids were examined through EXAFS. The X-ray absorption spectra at each metal edge of the bimetallic samples were collected on the Exxon beamline X10C. The EXAFS data of both edges were simultaneously analyzed employing a program developed at the Corporate Research Laboratories of Exxon [Via et al., *Cat. Lett.* **5** (1990) 25]. In each case mixed metal shells were observed, confirming the formation of intermetallic colloid systems. Furthermore, in the RhPt and Rh_4Pt colloids, the total coordination number of rhodium is less than that of platinum indicating that on the average rhodium is segregated to the surface of the cluster particles. In the Pd_2Cu colloid, a similar segregation effect is noted whereby the overall coordination number of copper is less than that of palladium indicating that copper tends to reside on the exterior of the cluster.

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The Investigation Through EXAFS of Highly-Dispersed, Supported Pd Catalysts

X10C

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For supported metal catalysts in which the metal is extremely highly dispersed, the determination of the particle size is often difficult. In many cases, even with high resolution electron microscopy, it is not possible to detect the metal particles on the oxide-support. Through EXAFS it is possible to determine whether the metal distribution is on an atomic level or whether metal clusters are still present.

The X-ray absorption spectra of two highly-dispersed Pd catalysts (0.5 and 1% Pd on Al_2O_3), each prepared via a different synthesis route, were measured on the Exxon beamline X10C. The Fourier-transformed EXAFS spectra clearly show that for the 0.5% Pd/ Al_2O_3 catalyst two shells are present (O and Pd) and for the 1% Pd/ Al_2O_3 catalyst only a single O-shell is observed. These results indicate that the Pd metal in the 1% Pd/ Al_2O_3 catalyst is dispersed as single, isolated atoms whereas the Pd metal in the 0.5% Pd/ Al_2O_3 catalyst is still found in clusters.

X10C CU AND NI K-EDGES STUDY OF THE REDUCTION OF SILICA SUPPORTED NI-CU PREPARED BY ION EXCHANGED

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The conventional preparation of a supported metal catalyst involves wet chemistry of metal ions at an oxide support surface followed by subsequent thermal treatment in oxidizing or reducing atmosphere. The nature of the interaction of the metal ions with the support is a key parameter to control the particle size and the metal composition in the case of bimetallic particles. Very little is known on how this ion-support interaction affects the final state of catalyst composition. Along this line, a study of the preparation parameters on the reducibility of the metal precursors in silica supported nickel-copper bimetallic catalysts, Ni-Cu/SiO₂, has been initiated this year.

Despite the complete miscibility of nickel and copper in the whole range of composition, some difficulties due to the homogeneity of the deposition and the different reducibilities of nickel and copper ions have to be overcome at the preparation level or during the activation steps. In monometallic systems, it is recognized that a very weak metal ion-support interaction leads to a large distribution of particle sizes. Conversely, a strong interaction leads to small particles with a narrow size of distribution. The major drawbacks are low reducibility and specific surface compound formation like, for instance, nickel silicates that forces the metal segregation at the ionic state. A monitoring of the catalysts structure at the primary stage of elaboration has been initiated for nickel¹ and, last year, for copper.

The previous study at the Cu K-edge shows that various copper complexes ion exchanged on silica form surface complexes directly linked to the silica through two Cu-O-Si bridges. This year, it has been shown by monitoring the edge during the reduction that the $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ copper ion exchanged complex undergoes a stepwise reduction from +2 to +1 and +1 to 0. This demonstrates that the two dihydrogen consumption peaks of equal intensity measured by TPR are due to the same species and not two different phases. The $[\text{Ni}(\text{en})_3]^{2+}$ are reduced in a single step to metal at a temperature of 650°C. In presence of Cu, Ni can be reduced simultaneously with the second reduction step of Cu, i.e., simultaneously with the Cu⁺ ions. This occurs only if a calcination step is performed before reduction. Full data analysis requires to take into account multiple scattering effects from the Cu-O-Si bridges. This is in progress using the FEFF 5 software for multiple scattering simulation.

- 1 M. Che and L. Bonneviot, *Pure Appl. Chem.*, **60**, 1369, 1988; O. Clause, M. Kermarec, L. Bonneviot, F. Villaine and M. Che, *J. Am. Soc.*, **114**, 4709, 1992.
- * en = ethylenediamine (bidentate ligand)

X10C

CU AND RU K-EDGES STUDY OF COPPER ION ANCHORING SITES IN SUPPORTED BIMETALLIC RU-CU CATALYSTS OF VARIOUS COMPOSITION

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In bimetallic supported catalysts, one of the questions is to know the role of the metal-support and gas-support interfaces in the metal segregation process. In the metal-support interface, it has been claimed that ions (chromium, iron...) can act as anchor for the nuclei from which the metal particles grow. As a consequence, the particle sizes are smaller and the size distribution is narrower than without anchor. Though the effect has been widely documented, there is no direct evidence that those ions are located at the metal-support interface. To investigate this particular point, a model silica supported RuCu bimetallic has been studied. These two metals are immiscible and copper is expected to segregate at one or another of the interfaces cited above. To force the copper to be located at the metal-support interface, the Cu²⁺ ions (0.36 wt%) were first ion exchanged on silica on which, subsequently, was impregnated a reduced precursor of ruthenium, i.e., a carbonyl cluster, [Ru₆C(CO)₁₆]²⁻. Three catalysts of Ru/Cu molar ratio of 9, 3 and 1 were prepared. The reduction process under H₂ flow was monitored at the Cu and Ru K-edges while the temperature was linearly ramping up to 490°C.

The result of this year confirms that, in presence of ruthenium, the Cu²⁺ ions follow a different reduction pattern than without Ru and shows that this pattern is the same for the different Ru/Cu investigated here. Half of the Cu²⁺ ions are directly reduced to Cu⁰ at 290°C instead of being all reduced at the +1 oxidation state without Ru. The unreduced part is finally, reduced at the +1 oxidation state when 490°C is reached while, in absence of Ru, copper is fully reduced. Interestingly, the fraction of copper remaining at the +1 oxidation state after reduction is approximately constant for Ru/Cu = 9 to 1. Conversely, the ruthenium cluster decomposition is triggered by the reduction of copper and starts at 170°C, that is, about 50°C lower than without Cu. This latter point could be explained by the hydrogen split over from reduced copper or decomposed Ru clusters. The unreduced copper is more likely explained by its location at the metal-support interface where hydrogen is not effective to fully reduce copper. Since the fraction of unreduced copper is invariable, it seems that the copper ions are most probably paired (non EPR active), and each are interacting with ruthenium clusters. To complete this study, one should study the effect of copper loading on its reduction pattern.

X10C

SINGLE CRYSTAL EXAFS STUDIES OF *C. pasteurianum* NITROGENASE

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Nitrogenase catalyzes the reduction of dinitrogen to ammonia. Substrate reduction is thought to occur at the M-center, a MoFe₇S₆ cluster. Accurate dimensions of the M-center are important for synthesis and to understand possible changes during the catalytic cycle. X-ray diffraction structures for Mo-Fe proteins are progressing rapidly, and models for the M-center structures have been presented. However, given the limited resolution (2.2 Å), the r.m.s. error in the atomic positions of these models is about 0.2-0.3 Å. Since changes of metal-metal distances on the 0.1 Å scale are chemically significant, more accurate cluster dimensions are important. Here, we report newly measured Fe K-edge EXAFS on single crystal Mo-Fe proteins. The result agrees with our previous EXAFS analysis. The observed amplitude changes in crystal EXAFS spectra are geometrically consistent with the crystallographic model. This study allows us to define average M-center distances with better accuracy.

Figure 1. (Left) Approximate orientation of the long axes (T_N) in the M centers of Mo-Fe protein unit cell. (Right) The Fe K-edge Fourier transforms for solution (dashed) and crystal samples (solid).

The comparison of Fourier transforms from single crystal and solution samples is shown in Figure 1. The spectrum was taken by orienting the crystal in such way that photon E vector is in the crystal bc plane, and parallel to b axis. Similar to the solution sample, the spectrum is dominated by Fe-S and Fe-Fe interactions at 2.28 Å, and 2.61 Å, as well as the long Fe-Fe, Fe-S, and Fe-Fe distances at 3.7, 4.2, and 4.7 Å. The 2.61 Å Fe-Fe interaction gets stronger in this orientation, while the Fe-S signal intensity is isotropic, consistent with 3 Fe-S bonds at nearly right angles to each other in the M-center. The 4.7 Å Fe-Fe interaction is much stronger in this orientation, which suggests that the 4.7 Å Fe-Fe interactions must be close to the cluster's long axis. This result agrees with the recent crystallographic model, in which the longer Fe-Fe vectors are about 15° ($\cos^2 15^\circ = 0.93$) away from the cluster long axis (3-fold). However, the 2.61 Å Fe-Fe distance is much shorter than the crystallographic value (2.87 Å), and suggests that crystallographic models need to be further refined.

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Exxon has instituted a program in the area of phytoremediation: the sequestering of heavy metal contaminants by plants. Plants called "hypo accumulators" sequester large amounts of metals such as Pb and Cd from soils.¹ Potentially this ability to accumulate metals can be used to cleanup metal contaminated sites and ground water. In order to realize this goal a greater understanding of how the plants are able to do this is required.

A program to elaborate this mechanism has been instituted with Rutgers U., with Exxon providing the characterization of the mineral phase of accumulated Pb in plant roots and Rutgers providing the botanical expertise and the Pb accumulating plants (*Brassica*). Preliminary experiments have identified Pb carbonates and phosphates as the mineral phase present after Pb has been accumulated under controlled conditions. Electron microscopy, electron spectroscopy and infrared spectroscopy has been used to chemically identify the mineral phase and to locate it spatially in the root tissue. Pb accumulation by corn plants has been studied, but both the nature of the deposited phase and its location within the plant remain in question.²

To augment the above program we propose to accomplish a set of beamline experiments to follow the accumulation of Pb with time. The XAFS of Pb will be analyzed to yield information regarding the initial binding of the Pb to plant tissue and subsequently to watch the nucleation and growth of the inorganic phases. This will be done over a period of approximately 24 hours with edges recorded every two hours. It is expected based on previous experiments in the laboratory that this period of time will cover the interesting Pb accumulating periods. The XAFS information will be combined with the other characterization and botanical data to build a complete picture of the process. It is also envisioned that additional metals will be investigated based on the success of the first experiment. At this point several preliminary lead edges have been collected to demonstrate feasibility.

¹ Baker, A.J.M., Brooks R.R., *Biorecovery*, **1**, 81-126 (1989)

² Malone, C., Koeppel D.E., and Miller R.J., *Plant Physiol.*, **53**, 388-394 (1974).

IN SITU MULTIELEMENT XANES STUDY OF THE FORMATION AND REDUCTION OF THE OXIDE FILM ON STAINLESS STEEL

X10C

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The effectiveness of *in situ* multielement XANES for studying the passivation of alloys has been demonstrated. By simultaneously windowing the appropriate K α fluorescence lines with a 13-element germanium energy-dispersive detector it is possible to measure concurrently the behavior of different alloying elements during electrochemical polarization. A thin film of stainless steel (100Å) was stepped between -1.5 and +0.4V(MSE) (the transpassive region of chromium) in a pH 8.4 borate buffer. On the first oxidation, no metal was lost and iron and nickel showed some oxidation. On reduction, significant iron and a barely detectable quantity of nickel dissolved. During the second oxidation, some chromium and a smaller fraction of nickel dissolved.

In situ multielement XANES enables potential and time-dependent studies of the interplay of elements in alloy passive films. Using thin film metal substrates to confer surface sensitivity, both the degree of oxidation and the amount of material lost in dissolution can be determined.

Figures: X-ray absorption edges of the constituents of stainless steel measured in the sequence Cr, Fe, Ni at each applied potential. No normalization or background subtraction has been carried out so edge heights reflect the amount of each element present.

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X10C

Probing the structural chemistry of the ZDDP mediated oil/steel interface in relation to thermo- and tribo-chemical reactivity

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For some time zinc dialkyl dithiophosphates (ZDDP) and related compounds have been used as anti-wear additives in lubrication oil formulations. However, the structure of ZDDP at an oil/steel interface and, in particular, its mechanistic action as an anti-wear additive, are far from understood. Improving our knowledge of this interfacial system is bound to contribute to the development of the next generation of clean technology additives for lube oils. We have been using [1] soft X-ray absorption spectroscopy in the energy region around the O K-edge and the Zn and Fe L-edges to examine the changes in interfacial chemistry involved in the decomposition of ZDDP containing lube oils adsorbed on polished mild steel. Our work reveals evidence for a cationic exchange process between Fe^{2+} in the surface oxide, and Zn^{2+} in the ZDDP, that takes place at the oil/metal interface under ambient temperatures. We have followed this reaction in-situ during sample heating from 25-150°C and have been able to monitor the thermal decomposition process:

- o the sub-surface structure, as revealed from the fluorescence yield spectra, shows a decrease in the intensity of the Zn L-edge threshold upon increasing temperature.
- o the total electron yield spectra indicate an increase in the concentration of the Fe at the surface.

The interfacial ion exchange process was found to be reversible below c.a. 80°C.

[1] G.P. Hastie, K.J. Roberts, D. Adams, D. Fischer and G. Meitzner, Jpn. Journal Applied Physics Vol. 32 (1993) Suppl. 32-2, 407-409

X10C

Identification of pre-melting behaviour in oriented thin films of normal alkanes using polarised ultra-soft X-ray absorption near-edge spectroscopy

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The crystal science and engineering of long chain hydrocarbons is of considerable interest in view of their role in the petrochemicals, natural oils and fats as well as in organised biological systems such as lipids and proteins. Recently, we have carried out a series of temperature dependent studies on alkane thin films (ca 200 nm thick) using NEXAFS spectroscopy at the C K-edge, with beamline U1, in order to determine the structural changes taking place within the systems prior to melting. Using grazing incidence (20°) and normal incidence (90°) scattering geometries with respect to the oriented thin films (prepared by vacuum evaporation onto Si (111) wafers) the orientation of the chain with respect to the substrate is determined. The effects of pre-melt structural disorder, as the temperature is increased, was observed as an increase/decrease of the relevant transition resonance. Using both electron yield and fluorescence yield detection allows the pre-melt processes occurring on the surface (ca. 2 nm) and in the bulk (ca. 200 nm) to be, respectively, monitored simultaneously.

Our studies indicate that the longer even n-alkanes ($\text{n-C}_{46}\text{H}_{94}$, $\text{C}_{50}\text{H}_{102}$ and $\text{C}_{60}\text{H}_{122}$) undergo bulk melt at the melting point with structural disorders becoming incorporated several degrees below the melt whilst the surface retains its structure until two degrees above the melt. This process appears reversible with the surface freezing out above the bulk freezing point. The studies on the shorter alkanes show that the structurally distinct groups found in the bulk crystals are maintained in the thin films; with $\text{C}_{26}\text{H}_{54}$ forming a triclinic structure, $\text{C}_{34}\text{H}_{70}$ and $\text{C}_{36}\text{H}_{74}$ forming monoclinic structures and $\text{C}_{37}\text{H}_{76}$ an orthorhombic structure. For the short even alkanes, which all exhibit rotator phases, there is evidence of structural disorder being incorporated simultaneously in both the bulk and on the surface several degrees below the melt. In contrast to the longer homologues, the shorter alkanes do not become reoriented upon recrystallisation after the melt.

IN SITU XAS STUDY OF ADSORBED Pb ON CARBON SUPPORTED Pt

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The adsorption of Pb on Pt is very interesting in that the so-called underpotential deposition (UPD) region can extend over about a volt. Furthermore, Pb is adsorbed or incorporated into the surface oxides on Pt at positive potentials. Cyclic voltammetry in the UPD region on Pt(111) reveals rather complex behavior with several current peaks. These effects have been ascribed to surface phase transformations, different adatom-adatom interactions, or to changes in the electrosorption valency. Characterization of these Pb layers is difficult since they are disordered, except at very negative potentials. X-ray absorption spectroscopy (XAS), since it probes short range order, is an ideal method for studying disordered systems. Considerable enhancement of the XAS signal has been achieved in the case of UPD Cu on Pt by doing the experiments on carbon supported Pt. In the present study the adsorption of Pb on carbon supported Pt was studied over the potential range -0.24 V to 1.15 V SCE. Data were collected by windowing with a single channel analyzer (SCA) on the Pt L_3 fluorescence line obtained from a Canberra 13 element germanium energy dispersive detector. The XANES in the UPD region indicate the adsorption of neutral Pb species. Figure 1 shows Fourier filtered EXAFS data at various potentials in the UPD region. The data in Fig. 1 were taken successively at -0.24 V, -0.15 V and 0.25 V. It is evident that there are large changes in the EXAFS with potential. Analysis of the data are given in Table 1. The data indicate that Pb-Pb interactions occur only at negative potentials. There was no evidence for adsorption of O species from the electrolyte.

Table 1. Fitting parameters for data in Fig. 1.

Shell		Potential (V SCE)		
		-0.24	-0.15	0.25
Pb-Pb	N	2.2	0.8	
	R	3.05	2.99	
	$\Delta\sigma^2$	0.001	-0.02	
	ΔE_0	-3.8	1.6	
Pb-Pt	N	6.8	4.49	3.0
	R	2.86	2.83	2.82
	$\Delta\sigma^2$	0.018	0.01	0.007
	ΔE_0	-3.3	-1.1	2.33

N = Coordination number
 R = Coordination distance (Å)
 $\Delta\sigma^2$ = Debye-Waller factor (Å²)
 ΔE_0 = Inner potential shift (eV)

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Fig. 1. Pb EXAFS at -0.24 V (—), -0.15 V (---) and at 0.25 V (···).

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The ability of gallium to facilitate alkane dehydrogenation by solid acids, especially zeolites, is well known. Our study of Ga in several such systems has supported a model wherein it catalyzes recombinative desorption of H₂ via the formation of a gallane-like species, thus clearing catalyst surface and suppressing hydrogenolysis.

In situ spectroscopy of Ga deposited on ZSM5 zeolite showed that Ga was slowly reduced at least to the 1+ oxidation state above 500°C in H₂ or butane. In this condition, the gallium had only one oxygen neighbor detectable in its EXAFS spectrum. Upon cooling, the gallium returned to the 3+ oxidation state and occupied sites with tetrahedral symmetry inside the zeolite channels. Other work has shown H₂ evolution during cooling of an active Ga catalyst, and also the presence of mainly tetrahedral gallium in a quenched catalyst.

These results have led us in two directions. First, we are looking for evidence of similar redox chemistry of Ga on other refractory oxides. Second, we are investigating the concurrent formation and decomposition of hydride-like species by other elements, that might be useful in specific situations where atomic hydrogen should be cleared from catalytic surfaces.

Low Catalytic Activity of Platinum Supported on Zinc Aluminate

X10C

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Platinum metal dispersed on a refractory oxide carrier, for example Al_2O_3 , is an effective catalyst for carbon-carbon and carbon-hydrogen bond cleavage. Surprisingly, Pt supported on ZnAl_2O_4 was a very poor catalyst for these same reactions, apparently because the Pt was not reduced to the metal under conditions sufficient to reduce Pt supported on Al_2O_3 .

Measurements of the x-ray absorption spectra (XAS) of Zn and Pt, made on beamline X-10C, lead to this conclusion. First, the Zn spectra were valuable to guide the synthesis of authentic ZnAl_2O_4 , uncontaminated by ZnO. Second, x-ray absorption near-edge spectra showed that after a reduction in H_2 at high temperature, an amount of reduced Zn could be found that corresponded to an amount of Pt that remained unreduced in samples. We have hypothesized a surface species with the formula PtAl_2O_4 .

Both the spectroscopic and the chemical study of this system continues. Our immediate goals with XAS are to establish the oxidation state and physical environment of the unreduced Pt, and to identify the physical form of the reduced Zn.

X-11A

STUDY OF RARE EARTH WHITE LINES IN $\text{Re}_2\text{Fe}_{17}\text{N}_x$

M. Balasubramanian, J.I. Budnick, D. Brewster, T. Manzur, Y. Zhang, D.M. Pease (U. of Connecticut)

As one of the most promising permanent magnetic materials, the Rare earth (Re) compounds, $\text{Re}_2\text{Fe}_{17}$, has been a subject of widespread investigation. Recently, it has been found that the addition of nitrogen expands the lattice and brings about very large changes in magnetic properties. In an effort to explore the local electronic structure about the Rare earth we have prepared a number of $\text{Re}_2\text{Fe}_{17}$ systems and have nitrided them to a series of compositions up to $\text{N}=2.5$. We have obtained Re (Lu, Ho, Dy, Gd, and Sm) L_3 and L_2 XANES data on $\text{Re}_2\text{Fe}_{17}$ and $\text{Re}_2\text{Fe}_{17}\text{N}_x$. These XANES spectra probe, by a dipole allowed transition, unoccupied Re 5d states. Our results for the Dy L_2 edge are shown in the figure below. We observe a small, but definite *sharpening and narrowing* of all the white lines due to nitriding. The fact that this white line sharpening is observed due to nitriding in all the studied Re based systems is of interest. One possible simple interpretation is "narrowing" of the Re 5d band due to lattice expansion, an observation which may pertain to interpretations of magnetic alignment in these systems associated with interactions between Re and Fe d electrons. Further analysis and attempts to establish a correlation between the changes in white line area with nitrogen concentration and lattice expansion are in progress.

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RESIDUAL DISTORTION CORRECTIONS WITH A GLANCING EMERGENCE ANGLE EXAFS MEASUREMENT.

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The glancing emergence angle (GEA) technique allows x-ray absorption spectra to be obtained from the fluorescence of bulk samples with concentrated absorbing species; this is otherwise not practical because of severe self absorption effects. The GEA measurement removes the distortions due to self absorption by employing a geometry in which only that fluorescence leaving the sample at a glancing angle (~ 1 degree) is collected. This reduces the effective thickness of the sample by forcing the fluorescence originating deep within the sample to travel a long absorbing path, essentially eliminating this portion of the signal. An inherent disadvantage to the GEA technique is the relatively limited available signal for a condition of minimal distortion. However, we have completed calculations of the distortions in the coordination number and σ^2 for a given maximum emergence angle, which allows use of a greater emergence angle, thereby dramatically increasing the available signal, while still permitting precise determination of the EXAFS parameters. The calculations have been compared to experiment, with excellent agreement. The results are summarized in the Figure.

Figure: Distortions in the EXAFS parameters with a GEA measurement of a Cu standard of effectively infinite thickness, as a function of maximum emergence angle (Minimum emergence angle 0 degrees. Refraction is neglected). Solid curves are calculations; individual points are measured, with the distortion relative to transmission data from a Cu foil. (a) percent reduction in coordination number (b) percent reduction in σ^2 .

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SAMPLING DEPTH OF A GLANCING EMERGENCE ANGLE XAS MEASUREMENT

D.L. Brewre, D. M. Pease, J. I. Budnick (U. of Connecticut)

The glancing emergence angle (GEA) technique allows x-ray absorption spectra to be obtained from the fluorescence of bulk samples with concentrated absorbing species; this is otherwise not practical because of severe self absorption effects. The principle underlying the GEA technique is the limitation of the effective thickness of a sample by collecting the fluorescence leaving the sample at an emergent angle on the order of a degree, which forces the fluorescence emerging from deep within the sample to travel through a long absorbing path, effectively eliminating this portion of the signal. The ability to limit the sampling depth in this way also suggests the possibility of depth profiling experiments, in which different portions of the near-surface region are sampled by varying the maximum emergence angle. The sampling depth d_s may be defined as the depth at which some fraction, x , (say 90%) of the total received intensity comes from depths less than d_s . It may be easily obtained by setting the expression for the intensity integrated from the surface to d_s equal to x times the total intensity, and solving for d_s . The expression for the intensity integrated over a given range of depth within the sample was checked by measuring the step heights at several maximum emergence angles of three Cu films of different thicknesses, with excellent agreement between the measurements and calculations. The Figure shows results of calculations for the Ni edge of three materials, in which x was defined as 90%. The sampling depths are on the order of a μm or less, which is roughly the thickness required for a film in a conventional fluorescence measurement. One possible application in this regime is studies of the effects of surface grinding.

Figure. Sampling depth as a function of the difference between the maximum emergence angle and the critical angle, which is on the order of a half degree. The results illustrate the influence of both concentration of the absorber and type of atoms in the passive matrix (the ordered alloys in the figure are virtually identical except for the type of passive atoms).

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INVESTIGATION OF INTERATOMIC FORCES IN NiAl, CoAl, AND FeAl, USING EXAFS SPECTROSCOPY.

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It has been suggested that there is potential for acquiring information about interatomic forces in solids from the temperature dependent vibrational damping of the EXAFS, but this idea has been investigated only in limited cases. We have conducted a study of the temperature dependence of the transition-metal (TM) EXAFS in FeAl, CoAl, and NiAl in order to further investigate this potential, and explore possible correlations between interatomic forces and brittleness in these materials. We have developed an approach to the problem of investigating interatomic forces with EXAFS based on the general idea that the temperature-dependent mean-square relative displacements (σ^2) of different atom pairs in a given material possess different sensitivities to the various interatomic forces. This leads to the idea that multiple σ^2 's may be combined to form a system of equations indirectly involving the force constants in a Born-Von Karman model, from which a set of force constants may in principle be found by varying the force constants until a best fit to the experimental σ^2 's is achieved. Calculations of σ^2 's in NiAl were obtained from an existing force constant model, in order to study the feasibility of this approach. Sensitivities of σ^2 's to force constants were tested by systematically varying the force constants from the NiAl values and observing the effect on σ^2 . There were in fact significant differences in the sensitivities of different σ^2 's on the force constants, indicating significant potential for use of EXAFS to provide force-constant information in solids. Comparison of the aluminides showed that σ^2 of the first three shells surrounding the TM are very similar in FeAl and NiAl, while those of CoAl are distinctly different. The NiAl model calculations indicated that the TM EXAFS is sensitive primarily to changes in the two independent nearest-neighbor force constants, so that the differences between the EXAFS of CoAl and the other two materials may be attributed to differences in these two force constants. A fitting procedure involving the n.n. force constants was applied to the CoAl data; $\Delta\sigma^2$ between two temperatures was used, because of the difficulty in obtaining accurate absolute values of σ^2 . The best fit occurred with the n.n. diagonal force constant increased by ~35% relative to NiAl, and with the off-diagonal constant reduced to about 10% of the NiAl value (but with the exact amount uncertain). The increased diagonal force constant is consistent with increased resistance to shear in CoAl, in agreement with polycrystalline shear moduli of these materials. The estimated CoAl force constants were also used to calculate the atomic mean-square displacements, and the results were in agreement with electron diffraction results. The EXAFS results show a correlation between the interatomic forces, in particular the near-neighbor forces, and the brittleness, in that CoAl is distinct in terms of the force constants, and also the most brittle.

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X-ray Absorption Study of the Reaction of Titanium-Zirconium Alloy Thin Films on Si(111) Substrates

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Ti disilicides (TiSi₂) are often considered to be the optimal choice for contacts and interconnections in Very Large Scale Integrated (VLSI) circuits because of their low resistivity and high temperature stability. TiSi₂ has two different phases, a stable C54 phase with an orthorhombic face-centered structure and a metastable C49 phase with an orthorhombic base-centered structure. On the other hand, ZrSi₂ has only one stable phase: C49. Previous studies have shown that after annealing at high temperatures (700°C-900°C), Ti films react with the silicon substrates and form the C54 phase of TiSi₂. However, the C54 phase films are prone to islanding due to their high surface free energy. Thus, the surface roughness of the C54 phase films is much larger than that of the films with a C49 phase, which are formed by annealing at relatively lower temperatures (500°C-600°C).

In order to grow a smoother TiSi₂ film, which has larger areal coverage of the film on the Si substrate after high temperature annealing (>700°C), we deposited Ti-Zr alloy films on Si(111) wafers in order to use the ZrSi₂ structure to stabilize the C49 phase of TiSi₂. X-ray absorption experiments were performed on the 200Å thick (Ti_{0.9}Zr_{0.1}) alloy films annealed at temperatures between 500°C and 900°C. The Fourier transforms of the data are shown in Figure 1. It is obvious by comparison to previous Ti:Si data that only the film annealed the highest temperature (900°C) is in the C54 phase. Hence, Zr atoms do help to stabilize the C49 phase at the annealing temperatures of 700°C and 800°C, which represents an increase of about 200°C in the observed transition temperature from the C49 phase to the C54 phase. Atomic Force Microscopy measurements also showed that the surfaces of the alloy films are smoother than those of the Ti films annealed at 800°C and 900°C.

Figure 1, k^3 weighted Fourier Transforms for χ data (2.3-12.2 Å⁻¹) of (Ti_{0.9}Zr_{0.1}) alloy films deposited on Si(111) annealed at the temperatures from 500°C (bottom), 600°C, 700°C, 800°C and 900°C (top).

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MECHANISMS OF CHROMIUM(III) SORPTION ON SILICA. I: Cr(III) SURFACE STRUCTURE DERIVED BY EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS) SPECTROSCOPY

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Metal ion reactions at the solid/solution interface are important in an array of disciplines, and are of environmental significance as such reactions can greatly affect the risk imposed by metals. The structural environment of metals at the solid/water interface determines their potential for remobilization to the aqueous environment and the physical/chemical modifications of the sorbent. In this study, extended X-ray absorption fine structure (EXAFS) spectroscopy was used to discern the local structural environment of Cr(III) sorbed on silica. Chromium(III) formed a monodentate surface complex on silica, with a Cr-Si distance of 3.39 Å (Table I.). At the surface coverages investigated, a polynuclear Cr-hydroxide surface phase occurred with Cr-Cr distances of 2.99 Å, indicative of edge sharing Cr octahedra. Crystallographic parameters resulting from the measured atomic distances dictate that the surface phase was the γ -CrOOH type local structure. Environmental considerations of Cr(III) remobilization must therefore consider the chemical/physical properties of the monodentate surface complexed Cr(III) and surface nucleated Cr-hydroxide.

Table I. Structural information derived from EXAFS analysis: interatomic distances (r), coordination numbers (CN), and the Debye-Waller factors (σ). The 0 coordination and edge sharing Cr octahedra are reported along with the Cr to Si coordination shell.

	Cr-O			Edge:Cr-Cr			Si-Cr		
	r(Å)	CN	σ (Å)	r(Å)	CN	σ (Å)	r(Å)	CN	σ (Å)
γ -CrOOH	1.99	6.2	0.008	2.99	1.7	0.011			
$\phi=0.85^*$	1.98	5.8	0.012	2.97	2.7	0.005	3.38	0.9	0.008
$\phi=0.42^*$	1.90	6.1	0.013	2.98	2.4	0.006	3.40	1.1	0.008
$\phi=0.21^*$	1.98	5.9	0.012	2.98	3.0	0.007	3.39	1.1	0.009

*Potential surface site coverage for Cr(III) sorbed on silica (mols Cr/mol surface sites).

BUCKLED CRYSTALLINE STRUCTURE OF MIXED IONIC SALTS

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A detailed X-ray-Absorption Fine-Structure (XAFS) investigation of two mixed alkali halides $\text{Rb}_{0.76}\text{K}_{0.24}\text{Br}$ and $\text{RbBr}_{0.62}\text{Cl}_{0.38}$ was performed. The concentrations of the mixtures had been chosen to produce a single homogeneous phase for each, and it was checked by XAFS that the salts were randomly mixed on the atomic level. Detailed analysis of the data including multiple-scattering contributions revealed an rms buckling angular deviation of both mixtures from the average NaCl collinear structure of 7-9°. The angles are defined by three atomic positions determined through double and triple-scattering paths. These angles are new parameters which should be added to characterize the buckled crystals. Adding the parameters determined from XAFS as input into a molecular-dynamics (MD) simulation the structures of the mixed salts with their fluctuations about the NaCl structure are solved and displayed.

5 × 5 × 5 cluster of $\text{Rb}_{0.76}\text{K}_{0.24}\text{Br}$ as an output of XAFS measurements and MD simulations.

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X-11 A

Catalysis by Well-Defined Supported Metal Clusters: Ir₄/MgO

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A metal carbonyl cluster with a tetrahedral metal frame, [HIr₄(CO)₁₁]⁻, was prepared on the surface of partially hydroxylated MgO powder by adsorption of [Ir₄(CO)₁₂]. A supported Ir₄ catalyst was prepared by decarbonylation of the supported [HIr₄(CO)₁₁]⁻ by treatment in He followed by H₂ at 300°C. The surface structures were characterized by infrared and X-ray absorption spectroscopies. The decarbonylated cluster had an average Ir-Ir coordination number of 3.1, consistent with the hypothesis that the tetrahedral metal frame was largely retained after decarbonylation. The decarbonylated cluster was catalytically active for propane hydrogenolysis at 1 atm and 200°C. The catalyst that had been used for 1 day in a flow reactor was characterized by an Ir-Ir coordination number of 3.2. The lack of any significant change in the average cluster size indicates the stability of the supported catalyst, which is modeled as tetrahedral Ir₄ clusters. The rate of the propane hydrogenolysis catalyzed by the supported Ir₄ clusters at 200°C and at atmospheric pressure with a H₂/propane molar ratio of 2.5 was 0.02 molecules of CH₄ produced/(Ir₄ cluster · s). This is the first report of the catalytic activity of a well-defined supported metal cluster.

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X-11 A

IRIDIUM CLUSTERS IN NaX ZEOLITE CAGES: SYNTHESIS, CHARACTERIZATION, AND SELECTIVE CATALYSIS OF CO HYDROGENATION

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[Ir(CO)₂(acac)] in the pores of NaX zeolite was treated in CO at 1 atm and various temperatures and characterized by infrared and extended X-ray absorption fine structure (EXAFS) spectroscopies. The iridium precursor was converted predominantly into [HIr₄(CO)₁₁]⁻ at 70°C, and predominantly into [Ir₆(CO)₁₅]₂²⁻ at 175°C, as indicated by infrared spectra. The infrared spectra indicate that both of these clusters interact through ion pairing with the zeolite support. The chemistry of their synthesis in the zeolite cages parallels that on the basic MgO surface and in basic solutions. The zeolite-supported samples catalyzed CO hydrogenation at 20 atm and 250°C, having a relatively low activity in comparison with those of typical Fischer-Tropsch catalysts. The catalyst gave a non-Schulz-Flory distribution of hydrocarbon products with a maximum at C₁ and a relative maximum at C₄. Infrared and EXAFS spectra of the catalyst used with equimolar CO + H₂ feed showed that the predominant iridium-containing species was [Ir₆(CO)₁₅]₂²⁻. These clusters are suggested to be catalyst precursors. They are stabilized by the cages of the zeolite and by the CO atmosphere. The results summarized here are among the first to indicate the role of stabilized metal carbonyl clusters in CO hydrogenation catalysis at high temperatures.

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METAL-CONTAMINATED SOILS

M. J. Kelley (DuPont) and G. M. Lamble (X-11 PRT)

For several decades lead "motor mix" containing alkyl leads was used to enhance the octane of motor gasoline. Spills occurred at manufacturing sites, resulting in soil contamination. Oranoleads may present a greater hazard than inorganic lead compounds because many are volatile under ambient conditions. An appealing remediation strategy ("stabilization") is thus to convert them to non-volatile, non-leaching compounds when the contaminated soil is first disturbed.

As reported in a previous abstract, lead sulfide is a leading candidate for this role. Below are chi data for lead sulfide (top left), tetraethyl lead (lower left), soil contaminated by lead motor mix (lower right) and the same soil treated with a sulfide source and then aged 28 days under ambient conditions (top right, solid line). The dashed line in the top right figure is from an identical sample, except that cement was also added to enhance physical stability. Though the lead in the contaminated soil is clearly not entirely transformed to lead sulfide by the procedures employed here, certainly that is a major theme. As important, the utility of x-ray absorption spectroscopy in soil remediation studies is clearly evident.

The data were all obtained in fluorescence at the Pb L_{III} edge (13035 eV) on beamline X-11, with the samples cooled by liquid nitrogen. The chi functions are cut at $k = 10$ because a bromine edge interferes.

Glancing Angle EXAFS Studies of Copper "Pre-melting" at the Cu/Al₂O₃ Interface

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A number of experiments over the last few years have shown that surfaces play an important role in melting. Premelting near internal interfaces, however, have not been nearly as well studied. These concepts are important not only for understanding basic melting process, but also in technologies such as power metallurgy, crystal growth, and advanced composite materials. XAFS with glancing-angle x-ray reflectivity is performed to study the "pre-melting" behavior of Cu at buried interfaces in Cu/Al₂O₃ and other systems. The sample was fabricated by thermally evaporating 1000 Å Cu on 1 square inch quartz substrate inside an evacuated belljar at 10⁻⁶ torr. The sample was then quickly transferred to another vacuum chamber where ~700 Å of Al₂O₃ was e-beam evaporated over the Cu film. The goal of this experiment is to study the magnitude and anisotropy of vibrational amplitudes as a function of temperature below the melting point. XAFS and reflectivity measurement were done with x-ray polarization parallel and perpendicular to interface at various temperature. By varying the angle of incidence, it is possible to obtain depth-dependent structural information with depth varying from 10 Å to 50 Å. From these experiments the effect of the top several layers near the interface is expected. Earlier results implied large in-plane anharmonic motion in the top few layers. Here, we are repeating the measurements with higher-quality samples and more sophisticated analysis. Data analysis of

both the reflectivity and XAFS on these measurement is currently underway.

Fig.1 X-ray reflectivity measured at room temperature, 9.3 Kev, and having ϵ parallel to the interface.

X11A

EXAFS STUDIES OF ADSORBED COPPER ON CARBON SUPPORTED PLATINUM

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Underpotential deposited (UPD) monolayers of adsorbed metallic species can form on metals such as Pt at potentials that are positive to the reversible deposition potential for the metal. The study of UPD layers can yield insights into the nature of electrocatalysis and the structure of the electrode/electrolyte interface. EXAFS was used to study UPD Cu on Pt. The studies were done on high surface area carbon supported Pt to enhance the signal to noise ratio. In situ EXAFS spectra were obtained in $0.5 \text{ N H M H}_2\text{SO}_4 + 2 \times 10^{-3} \text{ M Cu}^{++}$ at 0.05 V SCE . The Fourier transform of the data is given in Fig. 1. Data analysis of the nearest coordination shells around the copper is consistent with Cu adsorption on Pt on the on top position with a Cu-Pt bond length of $2.67 \text{ \AA}$. The results also indicate that copper is also coordinated with three oxygens at a distance of $2.06 \text{ \AA}$ and one sulfur at a distance of $2.37 \text{ \AA}$. This indicates co-adsorption of bisulfate ions. The bisulfate is probably adsorbed on top of the copper where it facilitates charge transfer from the copper to the platinum and yields the adsorbed Cu^+ species that have been observed in XANES studies. A model of the adsorbed species is shown in Fig. 2.

Fig. 1. RDF for UPD Cu on carbon supported Pt.

Fig. 2. Model for three shell fit to the data. Bond distances are indicated.

IN-SITU XAFS OF HYDRIDE AND CARBIDE PHASES IN SUPPORTED PALLADIUM CATALYSTS

James A. McCaulley (Hoechst Celanese Research Division)

Pd K-edge XAFS was used to characterize hydride and carbide phases in supported 5% Pd/C and 5% Pd/ $\gamma\text{-Al}_2\text{O}_3$ catalysts.¹ Transmission measurements were made at 298 K. The average Pd particle diameter, from EXAFS and TEM results, is $26 \pm 8 \text{ \AA}$ in both catalysts. Pd particles in air-exposed catalysts were found to be ~98% converted to disordered Pd oxide; the remainder is in metallic cores (~6 Å diam.). Catalysts were reduced in-situ and cooled to 25°C in H_2 (partial pressure 26 Torr), yielding a hydride phase with a lattice expansion of $2.2 \pm 0.3\%$. See Figure 1. The stoichiometry, PdH_x ($x \sim 0.4$), agrees with previous reports of decreased H_2 sorption capacity, relative to bulk Pd, in supported Pd catalysts. Reacting the reduced 5% Pd/C catalyst with 1% $\text{C}_2\text{H}_4/\text{Ar}$ at 150°C for 20 min yields a Pd carbide phase with an average Pd-Pd distance 1.2% larger than in Pd metal. The PdC_x phase has a maximum carbon content about half that of bulk PdC_x , $x \sim 0.13$. The decreased carbon content of the Pd carbide phase in supported Pd catalysts is analogous to the decreased hydrogen content of the Pd hydride phase. PdC_x can be distinguished from PdH_x by its stability in the absence of H_2 . The rate of carbidization of 5% Pd/ $\gamma\text{-Al}_2\text{O}_3$ was found to be slower than that of 5% Pd/C; a detailed kinetics study is needed to determine the cause.

Figure 1. Nearest Pd-Pd distance, divided by that of metallic Pd, for supported particles in Pd catalysts in different chemical states.

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Genesis and Growth of Pt Particles on MgO: Characterization by X-Ray Absorption Spectroscopy and Infrared Spectroscopy

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Samples prepared by the reaction of $[\text{Pt}(\text{C}_3\text{H}_5)_2]$ with MgO powder were treated in H_2 at temperatures in the range 25–150 °C and characterized by X-ray absorption spectroscopy and infrared spectroscopy. As the temperature of treatment in H_2 was increased, the infrared spectra indicated the disappearance of bands attributed to the allyl ligands, and the sample became gray, the color characteristic of a supported metal. Adsorption of CO was characterized by a single infrared peak in the νCO region at approximately 2070 cm^{-1} , consistent with that observed for CO chemisorbed on metallic Pt. The Fourier transforms of the EXAFS functions measured near the Pt LIII absorption edge for each sample confirm the presence of metallic Pt, showing peaks at approximately 2.7, 3.8, 4.7, and 5.6 Å, consistent with the first, second, third, and fourth nearest neighbors in bulk fcc Pt. The EXAFS results indicate that the particle size increased from approximately 8 Å after treatment in H_2 at 25 °C, to about 9 Å after a similar treatment at 50 °C, to about 10 Å after treatment at 150 °C. The metal-support interface was characterized by two metal-support oxygen contributions, one at 2.18 Å and one in the range 2.7–2.9 Å. The total Pt-O coordination number decreased monotonically as the treatment temperature in H_2 increased. This result confirms that the fraction of Pt atoms in contact with the support decreased as the particle size increased. The normalized white line intensity passed through a maximum for the sample treated at 50 °C. Evidently electron density is affected by both the metal-support interaction and the particle size.

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EXAFS AND CATALYTIC ACTIVITY OF AgPt BIMETALLIC CLUSTER SUPPORTED ON NaY ZEOLITE¹⁾

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Platinum clusters with ca. 10 Å in size have been prepared as encaged in supercages of NaY zeolite by calcination and subsequent reduction treatments after ion exchange of $\text{Pt}(\text{NH}_3)_4^{2+}$ into NaY^{2+} . A series of bimetallic AgPt/NaY samples with Ag/Pt atomic ratios of 0, 0.11, 0.43 and 1.00 have been obtained by the reduction of silver after subsequent ion exchange of Ag^+ into the Pt/NaY sample. The result from measurements for ^{129}Xe NMR spectrum, and hydrogen chemisorption has indicated that the Ag atoms were put together onto the Pt cluster, with the surface enriched by Ag atoms. The extended X-ray absorption fine structure (EXAFS) of the bimetallic cluster measured above Pt L_{III} and Ag K edges has been analyzed with reference EXAFS spectra which were experimentally obtained from the metal foils and those for AgPt pair which were theoretically prepared by FEFF codes distributed by Rehr et al³⁾. The result of EXAFS data analysis has indicated the formation of AgPt bimetallic cluster with the core rich in Pt for the AgPt sample with Ag/Pt atomic ratio of 1.0. The catalytic activity in ethane hydrogenolysis into methane over the AgPt bimetallic cluster decreased from 1.6×10^{-3} to $1.6 \times 10^{-5} \text{ sec}^{-1}$ with the increase of Ag/Pt atomic ratio from 0.0 to 1.0, consistent with the EXAFS data.

Table I. Structural parameters of $\text{Ag}_y\text{Pt}_{7.1}/\text{NaY}$ catalysts from Pt L_{III}-edge and Ag K-edge EXAFS.

	atomic pair	$R^a/\text{\AA}$	N^b
$\text{Pt}_{7.1}/\text{NaY}$	Pt-Pt	2.77	6.0
	Pt-Ag	2.75	5.6
$\text{Ag}_{3.0}\text{Pt}_{7.1}/\text{NaY}$	Pt-Pt	2.76	0.3
	Pt-Ag	2.74	4.8
$\text{Ag}_{7.1}\text{Pt}_{7.1}/\text{NaY}$	Pt-Ag	2.76	1.4
	Ag-Pt	2.76	1.9
	Ag-Ag	2.81	1.6

^aNearest neighbor distance

^bNearest coordination number with uncertainty of ± 1 .

k^3 -weighted Fourier transforms of EXAFS function above the (a) Pt L_{III} edge and (b) Ag K edge of $\text{Ag}_{3.0}\text{Pt}_{7.1}/\text{NaY}$ (—), $\text{Ag}_{7.1}\text{Pt}_{7.1}/\text{NaY}$ (· · ·) and $\text{Ag}_{16.5}\text{Pt}_{7.1}/\text{NaY}$ (---).

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2D SAXS WITH HIGH SPEED CCD DETECTOR USING SYNCHROTRON RADIATION.

X11-A

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Detailed structural/morphological characterization of anisotropic polymers (e.g. fibers of films) can be accomplished with both two dimensional wide angle and small angle x-ray scattering (SAXS) experiments. A major experimental problem encountered in SAXS on conventional instruments is the inability to capture digital spectra in a very short time (minutes). Digitized spectra using a multiwire detector, however, require highly tuned systems and long path lengths (5-10 meters) because of the limitation in the resolution of this detector.

A new technique was developed using conventional pin-hole optics with a state-of-the-art charge couple device detector (Princeton Instrument Inc. 1124x1152 pixels) which has a spatial resolution of $25 \times 25 \mu\text{m}^2/\text{pixel}$. The setup, shown in Figure 1 was tested using the X11A beamline. The path length is only ~1 meter long. Calculations indicate that the detector is highly sensitive to the 8.04 keV ($\text{Cu K}\alpha$) radiation (equivalent to photon counting). Typical polyethylene terephthalate fiber SAXS pattern can be acquired in 20 minutes as opposed to ~16 hours using the conventional photographic technique.

High Resolution SAXS Apparatus

STRUCTURE/MORPHOLOGY CHARACTERIZATION OF CO AND COTBP AT ELEVATED TEMPERATURE.

X11-A

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X-ray characterization of CO (co-polyester of p-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA)) liquid crystal polymer particularly focusing on aperiodic nature of the chain sequencing has been extensively carried out [1]. These polymers are of commercial interest because of the melt processibility and improved properties over conventional random coil polymers. Even though there are continuing questions [2,3] on the structure of liquid crystal polymer at room temperature, detailed structure/morphology of LCP using wide angle (WAXS) and small angle (SAXS) scattering at elevated temperature and heat-treatment time has never been investigated.

Because of the high flux of synchrotron radiation, we have set up the newly built SAXS facility which will enable capturing of SAXS pattern in a very short time (minutes) [3], and carried out experiment on CO and COTBP (co-polyester of (HBA/HNA/terephthalic/biphenol) as a function of temperature. Preliminary results showed that additional small angle scattering (apart from voids scattering) can be observed at elevated temperature. Present work concentrates on quantifying the SAXS patterns as a function of heat-treatment and temperature.

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SELENIUM AND ZINC EDGE XAFS OF ZINC SULFIDE NANOCCLUSERS

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Spherical nanoclusters of ZnS, capped with 3-mercaptopropanoic acid (RSH) or benzeneselenol (SePh), were prepared by reaction of Zn^{2+} with varying ratios R of $(\text{S}^{2-})/(\text{RSH})$ or $(\text{S}^{2-})/(\text{SePh})$. The question of disorder induced by the sulfhydryl capping groups was addressed by plotting the Zn edge XAFS second shell coordination number vs. the cluster diameter as in Fig. 1. Upon comparison to the results of the calculated second shell coordination number of a zinc blende structure as a function of diameter, it is clear that capping reduces that number in a manner consistent with a disordered outer shell of thickness *ca.* 4 Å, depending upon the capping group. Further information on the binding mode of the capping group was found from Se-edge XAFS of samples of $\text{ZnS}_x(\text{SePh})_y$, one example of which is shown in Fig. 2. The Se is bound to one C (phenyl group) and two Zn atoms. This agrees with earlier results on S-edge XAFS and thus the group is primarily a bridging ligand between two Zn atoms at the surface of the cluster. NEXAFS of the Se-capped particles shows the presence of scattering from phenyl carbon atoms.

Figure 1 Second shell coordination number of Zn in capped ZnS samples.

Figure 2 Se edge transform at 100 K. Bulk SeZn (—), (SePh)SZn, $R=1.5$ (---) at 2x scaling.

THE NATURE OF THE FERROELECTRIC PHASE TRANSITION IN PbTiO_3

N Sikron (Hebrew U), Bruce Ravel (U of Wash.), E.A. Stern (U of Wash.), Y. Yacoby (Hebrew U), F. Dogan (U of Wash.), and J. Rehr (U of Wash.)

We have quantitatively measured the temperature dependence of the local distortions in PbTiO_3 crystals below and above the ferroelectric phase transition temperature (T_c) using X-ray Absorption Fine Structure (XAFS) measurements. Two probes, Pb and Ti, were used. The results were analysed by fitting parameterized theoretical XAFS spectra to the experimental results. The off-center displacements of the Pb and Ti change relatively little with temperature below T_c , decreasing faster near T_c . Above T_c , the displacements of the Pb and Ti atoms are 60% and 70% of their corresponding low temperature displacements. These results show that an essential element of order-disorder is present even in this nominally pure ferroelectric crystal displaying a soft mode and a dielectric constant typical of displacive ferroelectrics. The presence of the local distortions suggests that the displacements should have at least two length scales, one associated with the local distortions, the other with the order-disorder parameter.

The temperature dependence of the *a* and *c* unit cell dimensions. Solid lines represent the average dimensions obtained from X-ray diffraction. The x's and diamonds represent the *c* and *a* axis lengths obtained from the Ti-edge XAFS.

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X11A

Ga_{0.5}In_{0.5}P AND Ga_{0.5}In_{0.5}As THIN FILMS DEPOSITED ON GaAs AND InP, RESPECTIVELY, STUDIED USING EXAFS

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K. A. Bertness (NREL)

Epitaxial MOCVD thin-film alloys of Ga_{0.5}In_{0.5}P and Ga_{0.5}In_{0.5}As grown on GaAs and InP, respectively, substrates have shown spontaneous long-range ordering and band gap reduction under particular growth conditions. A liquid nitrogen cooled total-electron-yield detector is used to investigate the EXAFS contribution of first, second and third nearest neighboring atoms in these single-crystal samples to determine the details of their short-range ordering.

Results from the gallium second nearest neighbor contribution in numerous Ga_{0.5}In_{0.5}P on GaAs samples have been scrutinized. One ordered sample, grown at 670 C, has revealed a sizable difference in the second nearest neighbor peak region at two perpendicular orientations of the sample crystal. These orientations highlight different atoms in the plane of growth indicating that different quantities of elements are present along different crystal axes. This result correlates to the (111) superlattice-type growth indicated by TEM measurements.

All other samples, grown at a variety of temperatures above and below the ideal growth temperature of 670 C, do not reveal significant differences in the second shell, although some samples emit TEM superlattice peaks, and all show some degree of band gap reduction. This may indicate that the percentage of domains of spontaneously-ordered material is small compared to other domains, but still significant to the band gap. Fitting has shown in some of these samples a predominance of disordering, and possibly a tendency for Ga to clump around Ga in the second shell. Samples with Zn added to cause deliberate disordering do not reveal a difference in the two orientations, as expected. More precise analysis is underway and results from recent EXAFS at Ga and As K-edge from Ga_{0.5}In_{0.5}As on InP will soon be presented also.

X-11 A

Fe-protein Interactions in Genetically Engineered and Natural Ferritins

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Ferritin proteins control the rate of conversion of FE(II) in solution protein coat. In nature, the proteins concentrate iron many orders of magnitude above that of the free metal. Native ferritins are composed of mixtures of similar polypeptides which combine to give proteins that vary in mineralization rate by factors of up to 100. Recently, using recombinant protein, an Fe(III)-tyrosine (protein side chain) complex was observed to be associated with rapid mineralization in the early stages. The iron environment in solutions of the protein with the Fe(III) complex present, as well as solutions of slow mineralizing proteins, and proteins with slow mineralization rates induced by genetic engineering, was measured to determine the effects of changes on the ferritin protein on the mineralization. Analysis is still in progress.

Ferritin from plants and microorganisms have different minerals than in animal ferritin, due to the high phosphate content of bacterial cells and chloroplasts. Ferritin in plants is found in plastids. Pea ferritin iron cores were shown by EXAFS to have the same Fe-P and Fe-Fe distances found in the bacterial ferritin cores previously measured on X-11, emphasizing the importance of the environment at the time of mineralization on the mineral formed.

This research was supported in part by NIH-DK 20251.

CHEMICAL ENVIRONMENT OF Mn ATOMS IN NANOSCALE MANGANESE OXIDE PHASES SYNTHESIZED IN APOFERRITIN

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The synthesis of nanoscale inorganic materials has drawn much attention in recent years because of their unusual structures and unique structure-related properties. Recently a novel method was developed to form nanoscale particles of manganese oxide (or possibly hydroxide) in the cavity of apoferritin.¹ To study the structure and chemical environment of these nanoscale manganese oxide phases, the x-ray absorption fine structure (XAFS) measurements were made on some samples prepared by the reported method. The samples were also characterized by transmission electron microscopy (TEM), electron paramagnetic resonance (EPR) spectroscopy and electron diffraction (ED). TEM micrographs revealed that the manganese oxide cores were spherical with a typical core diameter of about 70 Å. Electron diffraction analysis suggested that the manganese oxide cores are amorphous. A very broad single peak ($g=2.02$) was observed in the EPR spectrum. The Mn K XAFS data of the sample were collected in fluorescence mode at room temperature and those of reference materials ($[\text{Mn}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, MnO, $\text{Mn}(\text{acac})_3$, $\text{Mn}(\text{acac})_2(\text{H}_2\text{O})_2$, MnO_2) were collected both in fluorescence and transmission modes. Comparison of Mn K edge energies of the sample and the references strongly suggested that the oxidation state of Mn of the sample is +2 in contrast to the original report (Table 1).¹ Figure 1 shows the Fourier transform of the XAFS of the sample. Curve fitting analysis using $[\text{Mn}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ aqueous solution as a reference indicated that the first coordination sphere consists of 5.8 (2) oxygen atoms at the distance of 2.18 (1) Å.

Figure 1. Fourier transform of manganese oxide in apoferritin

Table 1. Comparison of edge energies

1. F. C. Meldrum et al., *Nature*, **349**, 648 (1991).

* This work was carried out at the beamline X-11A of NSLS and was supported by PLS, POSTECH, RIST and USDOE under contract nos. DE-AS05-80-ER 10742 (X-11) and DE-AC02-76CH00016 (NSLS).

EXAFS STUDY OF PHASE FORMATIONS OF COBALT SILICIDE AND COBALT GERMANIDE

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We have investigated the phases of Co thin films (200Å) reacting with atomically clean Si(100) and Ge(100) in UHV at annealing temperatures ranging from 200°C up to 800°C. Fourier transforms of Co K-edge EXAFS oscillations of Co/Si samples are shown in Figure 1. The as deposited sample is the same as metallic Co foil. The shift of first peak position from 2.2Å to 1.8Å for the annealing temperature of 275°C indicates the strong formation of Co-Si bonds at this temperature. The increase of the peak amplitude between the samples annealed at 275°C and 375°C indicates that structure has become more ordered as annealing temperature increases. Figure 1 also shows that spectra of the samples annealed at 575°C and higher are very similar. They are totally different from those annealed at lower temperatures. This implies the formation of a new phase and this new phase is stable at high annealing temperatures. The quantitative EXAFS structural parameters, i.e. the bond length, coordination number, and DW factor, were obtained by standard EXAFS fitting procedure. For samples annealed at 575°C and higher, the obtained structural parameters of the first three shells agree with those of the CoSi_2 phase (cubic CaF_2 structure). For the sample annealed at 375°C, our fitting results match well with the local arrangements of the CoSi phase (cubic FeSi structure). However, for the sample annealed at 275°C, EXAFS results indicate that there is a disordered CoSi phase because of lower coordination numbers and larger DW factors for the first three shells compared to those of the sample annealed at 375°C. In summary, for the Co/Si system, it is found that the CoSi phase (FeSi structure) is formed at 375°C through a very disordered Co-Si phase, which begins at least at 275°C, and the final CoSi_2 is formed beginning at 575°C. For the cobalt-germanium system, the Co_5Ge_7 phase is identified for Co/Ge samples annealed at 300°C and 450°C. The final CoGe_2 phase is formed at 600°C. These results have been correlated with the surface morphologies and sheet resistances of these thin films.

Figure 1. Fourier Transform of Co K-edge EXAFS (k^2 weighted) of $\text{Co/Si}_{0.8}\text{Ge}_{0.2}$ samples annealed at different temperatures. The transform range is from 3.0Å^{-1} to 13Å^{-1} .

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X11-A

Chemical Dynamics of Refractory-Metal Carbides Formation by Time-Resolved Diffraction

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The formation of refractory-metal carbides by combustion synthesis from their elemental constituents has been studied by time-resolved diffraction (TR-XRD) using a monochromatic focussed beam at X11-A. The reactions $M + C = MC$, where $M = Ti, Zr, Hf$ and Ta have been followed with a time resolution down to 50 ms. These metal carbides crystallize in the NaCl structure with a relatively simple (due to high crystal symmetry) diffraction pattern that can easily be identified and unambiguously be distinguished from the reactant metal pattern (hcp for Ti, Zr and Hf; and bcc for Ta). In contrast with the $Ta + C \rightarrow TaC$ reaction [1], the syntheses of the Group IV metal carbides do not exhibit the formation any intermediate phases within a time resolution of 100ms. Typically, arrival of the combustion front was detected by decrease in intensity of the Bragg peaks of the metal due to the Debye-Waller effect and, within a 100ms frame, the product carbide began to emerge. This was followed by a complete disappearance of the metal reactant in the next 100ms. Beyond that the metal carbide peaks shifted to higher angle, denoting lower interatomic spacings due to lattice contraction upon cooling. In the case of the TaC formation (Fig. 1a), the results show the formation of the sub-carbide (Ta_2C) phase as an intermediate as evident in the integrated intensity profiles shown in Fig. 1(b).

Fig. 1 (a) Selected TR diffraction scans of the $Ta + C \rightarrow TaC$ reaction;
(b) Normalized integrated intensity plots from the TR scans shown in (a) vs. time

1. E.M. Larson, et al., J. Mater. Res. **8**(7), 1533 (1993)

CHANGE IN HEME STRUCTURE OF CYTOCHROME C WHEN REDUCED WITH GUANIDINE AND CARBON-MONOXIDE

X11a

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The X-ray absorption fine structure (XAFS) technique was used to investigate the structural environment about the Fe-Heme site of cytochrome c in various forms. The oxidized sample was from SIGMA and then was purified so that the concentration of Fe ion not in protein was much smaller than the concentration of Fe ion in protein. The reduced cytochrome c sample was prepared by adding 2 folds Sodium dithionate to the purified oxidized protein. The sample reduced with 6M guanidine was always away from the air. The sample reduced with CO and guanidine was prepared by bubbling the reduced protein in 6M guanidine with CO in the bag full of argon.

The following figure shows the near edges of XAFS measured on above samples. We can see the edge energy (dotted line) of the oxidized sample is different from the one of the other three reduced samples. However, the XAFS of three reduced samples have different near edge structures even though they have same edge energies, indicating the denaturing of guanidine on reduced cytochrome c and the binding of CO to the guanidine-denatured reduced cytochrome c affected the Heme structure in cytochrome c. The near edge (dash line) of reduced protein in 6M guanidine has bigger pre-edge pip than the one (dot line) of reduced cytochrome c. The edge shape (solid line) of CO-combined reduced cytochrome c in 6M guanidine is very different from the one of other two reduced samples.

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SAXS STUDIES ON NYLON 6,6 FIBER MORPHOLOGY: I. EFFECTS OF SPINNING SPEED AND HEAT TREATMENT

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Establishing and understanding the correlations between fiber structure, properties and process control parameters are essential for tailoring fibers for specific end uses. With this aim in mind, we have undertaken a detailed study of the effects of spinning speed, drawing and heat treatment on Nylon 6,6 fiber morphology using Small Angle X-ray Scattering (SAXS). Meridional SAXS scans from Nylon 6,6 fibers spun at three different speeds (1200 yds/min, 3500 yds/min and 5300 m/min) and heat treated at different temperatures (-o- untreated, -□- 150°C, -◇- 180°C) are shown in Fig.1. The correlation function approach is used to calculate the average inter-lamellar spacing (L_p) and the constituent crystalline (L_c) and amorphous (L_a) domain thicknesses. While L_p increases with increasing heat treatment temperature, the changes in L_c and L_a follow different trends, depending on the spinning speed. Fibers spun at 1200 ypm and annealed at 150°C show a 10Å increase in L_c with practically no change in L_a . Both L_c and L_a increase by 5Å for fibers spun at 3500 ypm and annealed at 150°C. In contrast, high speed spun fibers (5300 ypm) exhibit only a slight increase in L_c and L_a . Annealing at 185°C, above the Brill transition temperature of 175°C for Nylon 6,6, results in a substantial increase in L_c and a decrease in L_a in all fibers, irrespective of spinning speed.

DEVELOPMENT OF MILLISECOND STOPPED-FLOW INSTRUMENTATION FOR TIME-RESOLVED SOLUTION X-RAY SCATTERING MEASUREMENTS.

M. Capel (Biology, BNL)

We have developed a rapid mixing device that permits facile millisecond time domain solution scattering measurements of macromolecular kinetic processes in solution. A commercial ultra-violet spectroscopy stopped flow device (Biologic SFM-5) was rebuilt for compatibility with x-ray scattering measurements in transmission geometry and integration with X12B control systems. The mixing system consists of three independently-programmable stepper-motor driven syringes, a miniature mixing chamber, and an x-ray transmissive microflow cell. The flow cell consists of a thermostated, rigidly mounted quartz capillary (0.25, 0.5, 0.75, 1.0 and 1.5 mm path lengths), sandwiched between two miniature ionization monitors, for in-line sample transmission measurement. Mixing dead-time for solutions of reasonable viscosity is 2-4 msec, with a minimum shot volume of 15 μ l per channel. Solution reservoirs hold 30 ml of reaction solution, delivering a maximum of 2000 shots between refills. The flow cell is physically buffered against convective contamination from previous shots and from pre-cell fluidics. An optional time-delay line (25 - 500 msec) may be installed between the mixer and the flow cell. The x-ray illuminated volume of the cell stands above a dead volume of $\sim 7 \mu$ l.

The figures below display bench mark tests of the facility. 15 ml of a 30 mg/ml solution of hen egg white lysozyme was loaded into channel one of the mixing device and buffer loaded in the second. At time zero, 50 μ l of buffer was fed through the flow cell at maximum stepping rate of 3 ml/sec. 17 msec after the onset of channel two action, the channel 1 syringe delivered 25 μ l of lysozyme solution to the mixer at 1 ml/sec. 5 msec after completion of the mixing sequence, our programmable 2D imaging frame store was commanded to acquire 25 5 msec, 25 25 msec and 25 100 msec duration data frames. The mixing and data collection sequence was iterated 500 times. The accumulated 2D data frames were corrected for detector counting nonuniformities and radially averaged about the beam center. A second sequence with buffer in both mixing channels was subsequently run. Corresponding buffer radial profiles were subtracted from the lysozyme solution profiles, with corrections for incident flux, sample transmission and detector and data collection dead times. The buffer-subtracted cumulative radial profiles from the first 5, 25, and 100 msec frames are displayed in figure 1 (all traces normalized to fixed monitor counts, w. arbitrary vertical offset). Figure 2 shows the corresponding guinier analyses from the data traces of figure 1 (w. arbitrary vertical offset). This device will be used for kinetic studies of macromolecular assembly and protein folding/unfolding.

FIG 1

FIG 2

AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
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4 of 5

CONFORMATIONAL CHANGES IN α_2 -MACROGLOBULIN FROM LIMULUS ASSOCIATED WITH BINDING OF TRYPSIN

M. Capel (Biology, BNL), W. Mangel (Biology, BNL), P. Armstrong (Bio Dept, U.Calif., Davis) & J. Quigley (Pathology, S.U.N.Y., Stony Brook)

α_2 -Macroglobulin is the major proteinase inhibitor in extracellular body fluids. It is a glycoprotein that physically sequesters a wide variety of aspartic, cysteine, serine and metallo endopeptidases. The sequestering interaction of the macroglobulin requires catalytically active proteinase. Complex formation is initiated by specific, limited proteolysis in the "bait" region of each globulin subunit. Following cleavage, α_2 -macroglobulin undergoes a conformational change which results in the formation of a recognition site for receptors found on different cell surfaces.

Critical steps in its function as a proteinase inhibitor are the conformational changes that occur between cleavage of the α_2 -macroglobulin by an active proteinase and the entrapment of that proteinase within the interior of α_2 -macroglobulin. We are using small angle solution x-ray scattering to characterize conformational changes in the α_2 -macroglobulin of the American Horseshoe Crab, Limulus polyphemus. The crab macroglobulin was chosen since it is found as a homodimer (of monomer molecular weight 185 kDa). It therefore represents an unstudied class of macroglobulin. Currently known forms of α_2 -macroglobulin occur as homotetramers with monomeric molecular weights equal to that of the Limulus macroglobulin.

Extensively purified Limulus α_2 -macroglobulin was reacted with varying amounts of trypsin and chymotrypsin under conditions known to result in complex formation, without proteolytic degradation of the macroglobulin. Solutions were concentrated, and the small angle x-ray radial scattering functions measured. Scattering measurements over a concentration range of 1-12 mg/ml manifested insignificant interparticle interference effects. Fig 1 shows the guinier analysis of macroglobulin-trypsin complexes scattering data at different stoichiometries (trypsin/macroglobulin: A:0, B:0.25, C:0.5, D:0.75, E:1.0, arbitrarily offset along vertical axis), and shows very significant compaction of the macroglobulin (reduction in radius of gyration, R_g) associated with proteinase binding. Note the linearity of the guinier plots of the 1:1 complex (E) vs. the upward curvature of the trace for the free macroglobulin (A). The complex consists of a well defined, monodisperse structure, whereas the free macroglobulin structure is more "open" and less monodisperse. The curvature of the guinier plots is not due to differences in aggregation in the free globulin since the forward scatter from all 5 guinier analyses are very similar. Figure 2 shows an overlay of the P(r) functions (sine-fourier transform of scattered intensity) from the same experiment. Intersection of the P(r) functions from different stoichiometries occurs at a single isospecific point indicating that two end states are involved in the sequestration reaction path. The forms of the P(r) curves also demonstrates the compaction of the macroglobulin structure resulting from proteinase binding.

fig 1

fig 2

Solution X-ray Scattering of GAL4(62*) and LAC9(61).

K.H. Gardner (MBB Yale), M.S. Capel (Biology BNL), and J.E. Coleman (MBB Yale)

Currently, sixteen yeast transcription factors have been identified that utilize a conserved metal-binding motif of six cysteines at the core of the DNA binding domains. This motif, CX(2)CX(6)CX(6)CX(2)CX(6)C, is generally located within the N-terminal region of these large (800+ aa) proteins. As well, several members of the class have a dimerization domain immediately C-terminal to this section; biochemical and biophysical data have indicated that this dimerization is manifested both when the proteins are free in solution and also when they are bound to their DNA binding sites. We have prepared truncated versions of two closely related members of this protein class (GAL4 and LAC9) for study by solution NMR. These fragments include the DNA binding domain and a portion of the dimerization domain. Previous NMR work on the GAL4 fragment indicated that enough of the dimerization domain had been lost that the protein remained monomeric in solution, while an X-ray crystal structure of the GAL4/DNA complex demonstrated dimerization upon binding to the UASG DNA site. In contrast, NMR data collected on a LAC9 fragment of similar length suggested that this fragment was dimerizing on its own without DNA. To provide an independent confirmation of these results, we performed small angle solution X-ray scattering on samples of the GAL4 and LAC9 fragments at the NSLS. By analyzing the data generated from these experiments to determine the radius of gyration of the proteins being studied, we were able to determine that both proteins were monomeric in solution at concentrations similar to the NMR studies.

Figs. 1 A,B show $P(r)$ traces of the GAL4 fragment (pH 5.8 & 8, respectively) calculated from x-ray solution scattering data. Figs. 2 A,B are corresponding $P(r)$ functions from the LAC9 fragment scattering data. The multiple modes (submaxima) in all traces show that both GAL4 and LAC9 are subdivided into well defined, spatially isolated (but connected) domains. The $P(r)$ modes at highest r are diagnostic for the degree of dimerization. The data indicate that LAC9 is almost totally dimerized at the concentrations used at both pH 5.8 and 8, in the absence of DNA. At pH 5.8 GAL4 showed somewhat less dimerization than at pH 5.8, confirming the NMR indications.

fig 1a $P(r)$

fig 2a

fig 1b

fig 2b

CHARACTERIZATION OF THERMAL EXPANSION IN THE AMORPHOUS PHASE OF SEMICRYSTALLINE POLYMERS USING REAL-TIME X-RAY SCATTERING

Peter Pengtao Huo (MIT), Peggy Cebe (MIT), and Malcolm Capel (NSLS)

We report on a novel methodology for determining the thermal expansion of the *amorphous* phase in polymers that can not be obtained in the 100% amorphous state. This property is needed for calculation of bulk thermal expansion for polymers used in composite applications where thermal expansion mismatch must be reduced. Real-time high temperature x-ray scattering is used to provide complete information about the thermal expansion characteristics of polymers, using poly(butylene terephthalate), PBT, as an example ^{1,2}.

Real-time WAXS experiments were done in transmission mode ($\lambda=0.91\text{\AA}$). The system was equipped with a one dimensional position sensitive detector. The sample to detector distance was about 50 cm, and the beam profile was treated according to pinhole geometry. National Institute of Standards silicon powder was used to calibrate the peak positions. The sample was inserted into a hot stage, and the WAXS data were taken in real-time as the temperature increased from 34°C to 224°C at 10°C/minute. Real-time and static SAXS experiments were performed with the system now equipped with a two dimensional position sensitive detector. The sample to detector distance was about 120 cm ($\lambda=1.28\text{\AA}$). Data were taken as the temperature increased to 235°C at 10°C/minute; each scan was collected for 30 seconds. Due to the isotropic nature of our sample, circular integration of the SAXS intensity was used to increase the signal to noise ratio.

WAXS is used to examine the crystal lattice thermal expansion coefficient. SAXS is then used to characterize the thermal expansion of the bulk sample from changes in the periodicity of lamellar stacks. One dimensional electron density correlation function analysis gives the temperature dependent long spacing, L , lamellar thickness, l_c , and degree of crystallinity. The thermal expansion coefficient of the amorphous phase is derived by combining room-temperature SAXS with real-time SAXS at elevated temperatures.

The thermal expansion for the long period, L , can be viewed as the contribution from the crystal and amorphous layers, of thickness l_c and l_a , respectively. L and l_c are obtained directly from the one dimensional electron density correlation function analysis. Using a lamellar stack model, $L = l_c + l_a$. At temperature, T , we write $l_a(T) = L(T) - l_c(T)$.

At elevated temperature, l_a can be written in terms of room temperature ($T=T_0$) values as $l_a(T) = l_a(T_0) (1 + \alpha_a (T - T_0))$ where α_a is the thermal expansion coefficient for the amorphous phase in the direction along the normal to the lamellar stack. From a plot of $[l_a(T)/l_a(T_0)] - 1$ vs. $T - T_0$ we find the thermal expansion coefficient for the amorphous phase. For PBT this value is $\alpha_a = 6.0 \times 10^{-4} / ^\circ\text{C}$, which is three times larger than the expansion of the crystal phase c -axis.

1. P. Huo, P. Cebe, and M. Capel. *J. Polym. Sci., Polym. Phys. Ed.*, **30**, 1459 (1992).
2. P. Huo, P. Cebe, and M. Capel. *Proc. Sixth Internl. Symp. Nondestructive Evaluation of Materials* (Plenum Press, New York) 1993 in press.

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REAL-TIME X-RAY SCATTERING STUDY OF POLYMER BLEND STRUCTURE

Peter Pengtao Huo (MIT), Peggy Cebe (MIT), and Malcolm Capel (NSLS)

We have used x-ray scattering to study structure of blends of poly(butylene terephthalate), PBT, with polyarylate, PAr, prepared over a very wide composition range. PBT is a semicrystalline polymer while PAr is non-crystallizable. Using small angle x-ray scattering, we have studied the location of the non-crystallizable PAr.

Small-angle x-ray scattering experiments were performed on melt crystallized PBT/PAr blends at room temperature. Films were examined in transmission mode using a system equipped with a two dimensional position sensitive detector. The sample-to-detector distance is about 120 cm, and x-ray wavelength is 1.28Å, and the beam profile at the detector was treated according to pinhole geometry. Each SAXS scan was collected for 15 min.

Lorentz-corrected intensity, I_s^2 , vs. s is shown in Figure 1 for samples melt crystallized at 200°C. Curve 1 is PBT homopolymer, and curves 2-5 represent the PBT/PAr blends 80/20 (2), 60/40 (3), 40/60 (4), and 20/80 (5). Relative to PBT, the position of the intensity maxima increases for 80/20 and 60/40, but there is a decrease in the position of the peak maxima for 40/60 and 20/80. There is also a large low-angle scattering in the blends (but not in the homopolymer) from interference of large-scale structures. This suggests that PAr is not located solely in interlamellar placement with respect to crystal lamellae of PBT. To confirm this view we compare the measured long period with that calculated by assuming interlamellar PAr placement.

The long period L obtained from the intensity maximum as a function of composition is shown in Figure 2 by triangles. The long period is nearly independent of composition. The long period can also be calculated ^{1,2} as though the PAr were all interlamellar, which results in the solid circles in Fig. 2. Measured and calculated long periods are the same only for low PAr fractions. As PAr fraction increases, an interlamellar placement for PAr becomes less probable. We conclude interspherulitic or interfibrillar PAr placement occurs for blends with PAr > 0.40.

Fig. 1

Fig. 2

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SAXS OF ACTIVATED CARBON

X12B

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Small-angle X-ray scattering from a sample of activated carbon was measured to ascertain the nature of the extremely large surface area (per unit volume). Measurements of N_2 absorption indicate a surface area of $3000 \text{ m}^2 \cdot \text{g}^{-1}$, larger even than the value expected if the material contained exclusively single graphite layers. SAXS from the activated carbon sample was measured on beam line X12B and on beam line X23A3 to cover the Q range 10^{-3} to 10^1 nm^{-1} . The figure on the left below shows the SAXS recorded by the X12B instrument, scaled to units of absolute cross-section per unit volume per steradian by matching with the data from the X23A3 instrument. A preliminary analysis of the distance distribution function, $p(r)$, from this data, calculated by the ITP program [1], is shown in the figure on the right.

1. O. GLATTER & O. KRATKY; *Small-Angle X-ray Scattering*, ©1982, Academic Press: London.

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X12B

A SEARCH FOR THE ORIGIN OF THE UNIQUE 4.61 Å MACULAR CORNEAL DYSTROPHY X-RAY REFLECTION: A.J. Quantock (St. Louis U) and M.C Capel (NSLS).

The corneal stroma is a connective tissue whose unique macromolecular architecture is essential for corneal transparency. Synchrotron X-ray diffraction patterns obtained from cornea have provided much information regarding the arrangement of collagen on the fibrillar and molecular levels, and its relationship with corneal proteoglycans.

Previously, at the Synchrotron Radiation Source (Daresbury, UK), we used a 12 cm camera with a radiation wavelength of 1.488 Å and documented a high-angle X-ray diffraction ring arising from a periodicity in the region of 4.61 Å. This reflection is unique to corneas with macular corneal dystrophy (MCD) (Quantock et al., *Cornea*, 11: 185-190, 1992). This hereditary disease invariably leads to visual impairment and can only be addressed by surgical intervention. The phenomenon of the unique MCD X-ray reflection was recently utilized to aid the postoperative diagnosis of a clinically ambiguous case of MCD (Quantock et al., *Eye*, 7: in press, 1993). Presently we aim to detect the 4.61 Å MCD reflection at the NSLS, and identify the structure which gives rise to the reflection.

Portions of four MCD corneas (2 type I and 2 type II) were bisected and four halves were incubated for 5 hours at 40° C in keratanase 1 (type II MCD), N-Glycanase (type II MCD), chondroitinase ABC (type I MCD) or enzyme buffer (type I MCD) before being frozen. At the NSLS, specimens were mounted between mylar in a specially-designed cell. Synchrotron X-ray diffraction patterns were obtained from 4 untreated and 4 enzyme treated MCD specimens (plus 4 normal human corneas) on beamline X12 at the NSLS. The pattern from the empty mylar cell was subtracted from the corneal pattern in every case. The experimental conditions were; SDD = 22 cm, $\lambda = 1.0936 \text{ Å}$ and $E = 2584 \text{ MeV}$. The 51.5 Å lamellar spacing of cholesterol myristate was used to calibrate the system, and the value for $S (\text{Å}^{-1})$ was noted wherever a peak occurred on a radial intensity trace. The S values were then converted to real space.

None of the normal corneas demonstrated a reflection in the region of 4.61 Å whereas all four of the MCD corneal portions did (type I MCD at 4.63 Å and 4.65 Å; type II MCD at 4.63 Å and 4.67 Å). The MCD reflection was greatly diminished following incubation with chondroitinase ABC or N-Glycanase, and partially diminished following incubation with keratanase I. It was still evident following immersion in the buffer.

This work provides direct evidence for our supposition that glycosaminoglycans are the origin of the unique MCD reflection, and indicates the involvement of both chondroitin/dermatan sulphate and keratan sulphate.

Supported by Research to Prevent Blindness, Inc.

CRYSTAL STRUCTURE OF YEAST TATA-BINDING PROTEIN AT 2.3Å RESOLUTION

D. Chasman and P. Sharp (MIT)

We had determined previously the structure of the TATA-Binding Protein from yeast at 2.6Å resolution by molecular replacement from crystals diffracting to a maximum resolution of 1.7Å. A new data set was obtained having useful data extending to 2.3Å with the FAST detector on beamline X12C at the NSLS. The resolution of data collection was primarily limited by decay of the crystals during exposure to X-rays. The previous model was refined against the new data by positional refinement in XPLOR with shells of data representing resolution ranges of 20-6Å, 20.0-2.6Å, 6.0-2.6Å, and 6.0-2.3Å sequentially. Additional refinement of the model was performed by simulated annealing followed by tightly restrained refinement of B factors for individual atoms. The current R-factor for the model to 2.3Å resolution is 23.3%. Omit electron density maps define the model in regions which were unresolved by the previous data at 2.6Å resolution. Displayed below is electron density from a simulated annealing omit map calculated at 2.3Å resolution and circumscribing the omitted peptide backbone and valine residue.

This work is sponsored by grants DRG-1112 and P01-CA14051 from the Daymon Runyon-Walter Winchell Cancer Fund (D.C.) and the National Institutes of Health (P.S), respectively.

CRYSTALLOGRAPHIC STUDIES OF HHA1 DNA METHYLTRANSFERASE

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Three crystal structures of HhaI DNA methyltransferase (M.HhaI) have been solved using the crystallographic data collected from beamline X12-C: (1) the structure of M.HhaI in complex with S-adenosyl-L-methionine at 2.5 Å resolution; (2) the structure of a ternary complex between M.HhaI, a 13-mer oligonucleotide containing its recognition target (GCGC) and S-adenosyl-L-homocysteine at 2.8 Å resolution; (3) the structure of a covalent complex between M.HhaI, a 13-mer oligonucleotide containing methylated 5-fluorocytosine in its methylation site and S-adenosyl-L-homocysteine at 2.8 Å resolution.

The DNA is located in a cleft between two domains of the protein. The large domain contains most of the conserved sequences among all DNA (cytosine)-5-methyltransferases. It provides the catalytic residues, binds the cofactor, and contacts the minor groove of substrate DNA. The small domain is responsible for the specific recognition of target DNA and interacts with the major groove. None of the usual motifs known to interact with DNA are present. Remarkably, the target cytosine has swung completely out of the DNA helix and protrudes into the bottom of the cleft where it is available for methylation.

Figure 1. Stereo drawing of α -carbon backbone of the M.HhaI and the bound duplex DNA. The target cytosine has swung out of the double-stranded DNA helix.

X12C

STRUCTURE ANALYSIS OF BULLFROG RED CELL L-SUBUNIT FERRITINS

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Abstract: Ferritin is a 24 subunit protein that controls biomineralization of iron in animals, bacteria and plants. Rates of mineralization vary among members of the ferritin family, particularly between L and H type subunits of animal ferritins which are differentially expressed in various cell types. To examine ferritin from a highly differentiated cell type and to clarify the relationship between ferritin structure and function, bullfrog red cell L ferritin has been cloned, overexpressed in *E. coli* and cocrystallized with both magnesium and manganese, a good analog of iron. Crystals were obtained in 50mM MnCl₂, 45% saturated ammonium sulfate, 0.1M sodium citrate, pH 6.3, and in 10 mM MgCl₂, 1M sodium tartrate, 0.1M sodium citrate, pH 5.5. Under both crystallization conditions, the crystals are tetragonal bipyramids in the space group I422 with unit cell dimensions $a=b=128\pm0.5$ Å and $c=181\pm1$ Å. Crystals obtained in the presence of manganese and ammonium sulfate diffract to 1.9 Å, while those obtained in the presence of magnesium and sodium tartrate diffract to 1.6 Å. The point group symmetry of the molecule is 432, as in mammalian ferritins (1). Isomorphous crystals have been obtained under similar conditions for a site-directed mutant with a reduced mineralization rate in which Glu 57, 58, 59 and 61 are all replaced by Ala. The structure of wild type L-subunit with magnesium has been solved by molecular replacement using the calcium salt of human liver H subunit (2) as the model. The R factor for the 2.15-8 Å shell is 0.22. The overall fold of human H and bullfrog L ferritins is similar with a r.m.s. difference in backbone atomic positions of 0.98Å. However, there are significant differences in the DE loop, the D helix and numerous sidechain positions, many of which are conserved. Analysis of higher resolution synchrotron data is in progress.

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X12C

STRUCTURE OF THE REGULATORY DOMAIN OF SCALLOP MYOSIN AT 2.8 Å RESOLUTION

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The regulatory domain of scallop myosin - the protein switch that turns on this myosin motor in response to Ca²⁺ binding - can be obtained by proteolysis of scallop myosin S1 (Kwon et al., PNAS, 1990, 87, 4771-4775). This domain is a stable three-chain complex (MW ~45 kD) of a 10 kD heavy chain, together with two light chains. Crystals of the complex in the Ca²⁺-bound form have the symmetry of the monoclinic space group P2₁, with unit cell dimensions $a=52.5$, $b=87.0$ and $c=55.5$ Å and $\beta=114.5^\circ$. There is one molecule per asymmetric unit, with a solvent content of about 54%.

The structure has been solved and refined to 2.8 Å resolution. The phases were determined by multiple isomorphous replacement with anomalous scattering. The light chains, as inferred from the amino acid sequences, have a "dumbbell-like" fold, similar to that of calmodulin. The "essential" light chain winds around the N-terminal portion of the heavy chain, while the "regulatory" light chain winds around the C-terminal region; both have a polarity opposite to that of the heavy chain. The heavy chain is folded into a single long α -helix, which is stabilized by the light chain interactions. The two light chains make contact with one another over a very limited region. The first loop of the regulatory light chain is occupied by a Ca²⁺/or Mg²⁺ ion, and the "specific" Ca²⁺-binding site, which is unusual, is located in the first loop of the essential light chain. The structure reveals a network of critical linkages between the Ca²⁺-binding domain and the rest of the complex. There is also a special sequence (the so-called "IQ motif") along the heavy chain starting with FQ in the essential light chain binding zone and IQ in the regulatory light chain binding zone. We have determined the structural basis for this sequence motif and have deduced some general features of calmodulin/light chain binding. The structure provides an understanding of previous mutagenesis studies of the light chains and is also a starting point for a detailed description of the transitions responsible for Ca²⁺ regulation.

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AG/SI(111) INTERFACIAL STRUCTURES

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We have continued our study of the interfacial structure between a Ag film and a Si substrate. We have previously shown features of the Si(111)-(7×7) structure are retained under a room-temperature deposited Ag film on a clean Si(111)-(7×7) surface. Upon annealing above 250° C, this interface transforms into a (1×1) structure.

Three different Ag/Si(111) samples were prepared. These were two room-temperature deposited Ag films on clean Si(111)-(7×7) substrates, one of which was annealed to 380° C after deposition to form the (1×1) interface, and a room-temperature deposited Ag film on a Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface.

Our prior study indicates the Ag/Si(111)-(7×7) and the Ag/Si(111)-(1×1) interfaces to be sharp, as opposed to the Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$) interface which is very rough. Models of the interfacial structure are currently being evaluated.

The figure shows the measured Si(1 0 L) crystal truncation rod for the Ag/Si(111)-(7×7) and annealed Ag/Si(111)-(1×1) samples.

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ISOTHERMAL THICKENING AND THINNING PROCESSES IN LOW MOLECULAR WEIGHT POLY(ETHYLENE OXIDE) FRACTIONS CRYSTALLIZED FROM THE MELT. 4. END GROUP DEPENDENCE

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ABSTRACT. A series of low molecular weight poly(ethylene oxide) (PEO) fractions with different molecular weights (MW=3000 and 7100) and end groups (-OH, -OCH₃, -OC(CH₃)₃ and -OC₆H₅) have been systematically studied. The end group effect on diffusional motion in the melt of these PEO fractions was characterized by self-diffusion coefficient measurements through nuclear magnetic resonance. Wide angle X-ray diffraction experiments indicated that the crystal structures of the PEO fractions with different end groups were identical during and after crystallization. The existence of nonintegral folding chain (NIF) crystals in these PEO fractions in a wide undercooling region was observed by time-resolved synchrotron small angle X-ray scattering, differential scanning calorimetry, and transmission electron microscopy experiments. The integral folding chain (IF) crystals were found to be formed through both thickening and thinning processes during and/or after the NIF crystallization. It was also found that with increasing molecular weight and size of the end group, the thickening and thinning processes were increasingly hampered. Of additional interest, the fold length of initial NIF crystals not only increases with crystallization temperature (or decreasing undercooling) for each PEO fraction as commonly observed in polymer lamellar crystals, but also changes with the size of the end group. The kinetics of transformation from NIF to IF crystals is explained through the chain sliding diffusional motion along the direction perpendicular to the lamellar surface, which is end group size dependent. Linear crystal growth rate data measured via polarized light microscopy confirmed that the existence of bulky end groups reduce NIF crystal growth rates for PEO(MW=3000) fractions. With increasing molecular weight, the end group dependence gradually vanishes due to the introduction of chain entanglement.

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X-RAY REFLECTIVITY: A TOOL FOR STUDYING THIN FILMS

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The performance of composite membranes, as measured by flux and selectivity, decreases over the lifetime of service. One model that explains this aging behavior is densification at the interface between the polytrimethylsilylpropyne (PTMSP) collection layer and the tetrabromo bisphenol A polycarbonate (TBBA-PC) selective layer. The relationship between the film thickness and density of the selective layer also remains undetermined. To confirm the theorized densification at the bilayer interface and study the density-thickness relationship a method was needed which could characterize films of 150 Å thickness, as well as their interfaces. As a first step we have demonstrated the ability to characterize the thickness, interfacial roughnesses and minute density gradients of thin model TBBA-PC films cast on silicon wafer substrates using x-ray reflectivity.

Reflectivity spectra were collected using different photon energies at Dow, the University of Akron, and the National Synchrotron Light Source. Reflectivity spectra were measured from the as-cast films and again after the films were aged by annealing in vacuum at 150°C for 24 hours. The as-cast film thicknesses were 216, 236, and 178 Å. All three as-cast films possessed a positive density gradient profile with the density increasing from the buried interface up to the free surface. The two thicker films could be modeled with the same density profile, while the thinner film required a 20% lower average density. The modeled density profiles were independent of photon energy. Contrary to expectation, after aging all three films were slightly thicker (x, y, z Å respectively), and less dense (x % on average), but still exhibited the positive density gradient. The roughness of the free surface and buried interface were also found to increase due to annealing. We are now ready to examine the cause of composite membrane performance degradation, in addition to many other questions relating to the characteristics of thin polymeric films and bilayers.

NEW PHASE IN FATTY ACID LANGMUIR MONOLAYERS*

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Recently, it has been found (using Brewster microscopy) that the domain shapes in fatty acid Langmuir monolayers undergo changes indicating a phase boundary within what had previously been thought to be the near-neighbor-tilted 'D' phase region. This transition is not visible in monolayer isotherms.

We have studied this region of the phase boundary using x-ray diffraction. We find that there is indeed a phase transition; for example, as shown in the figure, a substantial change in the diffraction pattern takes place between 10 dynes/cm and 15 dynes/cm in $C_{18}H_{37}COOH$ monolayers at 30°C. At 10 dynes/cm, the diffraction pattern (one in-plane peak i.e. $K_z=0$, one off-plane peak) is the well-known one corresponding to the 'D' structure described above; at 15 dynes/cm, there is no in-plane peak but only a broad superposition of at least two peaks. As the pressure is increased further, these peaks move down and ultimately reach $K_z=0$, which is the untilted 'Rotator-II' phase. We are now in the process of fitting data in the range 5-30 dynes/cm to determine if the best fit is to a next-nearest-neighbor-tilted phase or an intermediate-tilt phase.

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Diffraction intensities from a monolayer of $C_{18}H_{37}COOH$ at 30°C, at two pressures (as marked).

Magnetic scattering from Dy in Dy/Lu Alloy

X14A

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Introduction

A new polarimeter was constructed and tested on a Dy₄Lu₆ alloy studied earlier with neutrons. Magnetic scattering was observed via resonant enhancement (XRES) of the scattering amplitude for electronic dipole transitions near the Dy L_{III} absorption edge¹. The first-order harmonic was used to study the helimagnetic structure of the alloy at low temperature. The single-crystalline alloy was grown by molecular beam epitaxy at the University of Illinois. Film thickness is 2300Å. The film was grown on a sapphire substrate, with Mo and Y buffer layers.

Experimental Techniques

In order to separate magnetic from charge scattering, the polarimeter was mounted on the two theta arm of the X-14 goniometer. Since the polarization of the magnetically scattered component (π) is rotated 90 degrees relative to the incident σ -polarization, resolution of the two scattered polarization components allows for separation of the XRES and charge scattering. In order to detect a single polarization, radiation scattered from the sample is diffracted a second time from the polarimeter analyzer crystal, at a Bragg angle close to 45°. The polarimeter is then rotated through 90° about the scattered wavevector in order to detect the second polarization component of the scattered beam.

For our experiment, a 1mm horizontal slit was placed upstream of the beam optics to select an incident beam 97% polarized in the plane of the synchrotron orbit. The energy of the incident beam was 7.784 keV, and the analyzer crystal used was SrTiO₃ (222), which has a Bragg angle of 44.8° at this energy.

Results

The Dy (0,0,2+ τ) and (0,0,2- τ) magnetic satellites were seen in the analyzer π (out-of plane) configuration. At 15K, $Q(002)^+ = 2.54 \text{ Å}^{-1}$ and $Q(002)^- = 1.98 \text{ Å}^{-1}$. At 60K, $Q(002)^+ = 2.55 \text{ Å}^{-1}$, and the integrated intensity of the magnetic peaks has decreased by a factor of .78 from the 15K data. At 120K no magnetic satellites were visible. The satellites were not observed in the analyzer σ (in-plane) configuration at either temperature. These results are consistent with earlier neutron diffraction data taken at NIST. SQUID data taken at the University of Illinois indicated a Néel temperature of 90K.

¹E.D. Isaacs, D.B. McWhan, D.P. Siddons, J.B. Hastings, Doon Gibbs, Phys. Rev. B, **40**,

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Figure 1. Dy (002) Bragg peak and magnetic satellites at 15K in the analyzer π -configuration. Peaks at 2.21 and 2.28 Å⁻¹ are due to the sample Y buffer layer and Lu cap layer.

Figure 2. Close-up of the Dy (002)⁺ peak at 15K. Fit to a Gaussian with a flat background. Center at 2.54 Å⁻¹; FWHM = .0079 Å⁻¹.

BASAL PLANE SPIN-ORIENTATION IN SUPERCONDUCTING UPd₂Al₃

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We have determined the orientation of the ordered moments in the newly discovered^{1,2} heavy fermion superconductor UPd₂Al₃ using x-ray resonance magnetic scattering. We use the polarization selection rules of the resonance process for a dipole allowed transition (uranium M_{IV} edge), $d\sigma/d\Omega \propto (\epsilon_i^* \times \epsilon_s) \cdot \mu$, where ϵ_i and ϵ_s are the polarizations of the incident and scattered photons and μ is a unit vector along the direction of the ordered moment. Rotating the sample, and thus μ , through 180 degrees while keeping the (0,1,3/2) magnetic Bragg peak fixed along the scattering wavevector $Q (= k_f - k_i)$ results in a 100% modulation of the (0,1,3/2) intensity. This process is the magnetic analog to the polarized dispersion method described by Templeton, et al.³ The figure shows the data (open circles) corrected for absorption. Since the moment points somewhere in the basal plane whose normal is not along $Q_{(0,1,3/2)}$, the lineshape is asymmetric. From a fit of the data to the polarization dependence of the cross section (solid line) we determine that μ lies along the [h,0,0]. This measurement was performed on a high quality ($T_C = 2 \text{ K}$), single crystal (1 mm x 1 mm x ~ 5 μm thick) imbedded in a polycrystalline ingot.

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²K. Gloos, et al., Phys. Rev. Lett. 70, 501 (1993).

³Templeton, D.E., et al., Acta Cryst. A41, 133 (1985).

FIGURE. Ψ -scan in UPd₂Al₃ for T = 10 K. The open circles are integrated intensities for the (0,1,1/2) magnetic Bragg peak taken for different values of the azimuthal angle, Ψ , about the [0,1,1/2]. The solid line is a fit to the data of the polarization dependence of the resonant magnetic scattering cross-section.

MAGNETIC ORDER IN THE HEAVY FERMION SUPERCONDUCTOR UPt_3

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We have studied the antiferromagnetic order in the heavy fermion superconductor UPt_3 . Using x-ray resonance magnetic scattering at the uranium M_{IV} -edge we have measured the temperature dependence of the ordered moment ($0.02 \mu_B/U$ atom)¹. The $(1/2,0,2)$ magnetic Bragg peak intensity shows a sharp onset at $T_N=5$ K and grows linearly to $T=0.6$ K, which is the measured superconducting transition temperature in our sample. Below 0.6 K the $(1/2,0,2)$ intensity is suppressed linearly with temperature to $T=180$ mK, the base temperature of this experiment, where the magnetic scattering is reduced by $\sim 9\%$ from the intensity at $T=0.6$ K. The antiferromagnetic correlation length is not long-range ($\xi_{[1/2,0,2]}^{-1} = 0.013 \text{ \AA}^{-1}$) and remains constant for all $T < T_N$.

The reduction of the $(1/2,0,2)$ Bragg intensity below T_C can arise from one, or both, of the following possibilities: i) A rotation of the ordered moment, to which we are sensitive through the polarization dependence of the resonant magnetic scattering. ii) A suppression of the size of the ordered moment. Case i) can arise if, for example, there is a finite angular momentum component to the Cooper pairs (an effective magnetic field) which reorients the small ordered moments. Case ii) might arise from a competition between the two ground states for states at the Fermi surface. Implicit in both of these cases is that the superconducting order parameter is a vector quantity. Our results fit into the larger context of recent measurements in UPt_3 such as neutron scattering,¹ ultrasound attenuation,² and muon spin relaxation³ which point toward a reduced-symmetry superconducting order parameter (e.g., d-wave) in which antiferromagnetism plays a vital role.

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² A. Schenstrom, et.al., Phys. Rev.Lett. 63, 332 (1989).

³ G.M. Luke, et.al., Phys. Rev.Lett. 71, 1466 (1993).

FIGURE. Temperature dependence of the integrated intensity of the $(1/2,0,2)$ magnetic Bragg peak in UPt_3 . $T=0.6$ K is the measured superconducting transition temperature in our sample. The solid lines are line fits to the data above and below $T=0.6$ K, respectively. Inset: $\theta/2\theta$ scan through the $(1/2,0,2)$ magnetic Bragg peak (filled circles), giving an inverse correlation length $\xi_{[1/2,0,2]}^{-1} = 0.013 \text{ \AA}^{-1}$. The open circles show the higher-order ($\lambda/4$) component for the same scan.

PHASE IDENTIFICATION IN NUCLEAR MATERIALS USING MICRO-DIFFRACTION

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Nuclear technologies such as Argonne National Laboratory's Integral Fast Reactor (IFR) face a number of fundamental material issues related to small-scale structures. One example is the chemical interaction between metallic U/Pu/Zr IFR fuel and stainless steel cladding, which can degrade the cladding during reactor operation. To understand the kinetics and thermodynamics of these interactions, isothermal diffusion couple experiments were conducted between a binary U-10 at. % Zr IFR fuel alloy and a Ni/Cr alloy. Scanning electron microscopy (SEM) was used to determine composition profiles across the diffusion zone, but no crystallographic information could be obtained in this way. The diffusion zone consisted of nine distinct intermetallic phase regions including four multi-phase layers. Four of the regions were less than $5 \mu\text{m}$ in width. Thus, standard X-ray diffraction techniques would be unable to resolve the individual phases.

An earlier attempt to perform microscopic X-ray diffraction studies on this sample at beamline X-7A was limited to a collimated beam width of $50 \mu\text{m}$, such that several intermetallic phase regions were exposed simultaneously. The higher fluxes available at beamline X-14, though, allowed a collimation to less than $20 \mu\text{m}$, greatly improving the data collection efficiency.

In this study, a cross-section of the diffusion couple was polished and encapsulated in a newly designed double-containment holder filled with argon. Both containers were fitted with Kapton windows to view the sample and to allow a path for the X-ray beam. This holder provided both containment for the radioactive sample and an inert environment for the easily oxidized nuclear fuel.

The collimated beam was translated in steps across the diffusion zone. At each step, diffraction patterns were collected with a position-sensitive detector (PSD) that could detect X-rays over a 3° range of 2θ . The PSD was repositioned to cover the entire 2θ range of interest. As an example, Figs. 1 through 3 are PSD diffraction patterns centered on $56^\circ 2\theta$. Figure 1, taken near the U/Zr alloy, shows the tail of the $(111) \alpha\text{-U}$ peak at a high 2θ value. Ten micrometers closer to the Ni/Cr alloy (Fig. 2), this peak has been replaced by peaks for an intermetallic compound in the diffusion zone. A translation of an additional $10 \mu\text{m}$ (Fig. 3) results in the detection of a new set of phases. In this way, even though the intermetallic phase layers were very small and despite the complications of the multi-phase regions, the quantitative diffraction results verified the presence of most of the phases predicted from the SEM work.

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Figure 1

Figure 2

Figure 3

X-RAY AND NEUTRON CRYSTALLOGRAPHIC STUDY OF A SINGLE QUASICRYSTAL OF AlPdMn

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The purpose of this study has been to collect a large set of X-ray and neutron integrated intensities from single quasicrystals of $\text{Al}_{69}\text{Pd}_{22}\text{Mn}_{9}$. This combination is particularly useful here because b_{Mn} (neutrons) < 0 . For the neutron measurements a large (8mm^3) single "crystal", with a mosaic spread of 0.3° , was used to measure 513 symmetry-independent peaks. The X-ray data was collected on a $\sim 400\mu\text{m}$ sphere from the same batch of material. For $Q_{\parallel}$ (the laboratory Q) between $0.6\text{\AA}^{-1}$ and $9.0\text{\AA}^{-1}$ and $Q_{\perp}$ between $1\text{\AA}^{-1}$ and $1.75\text{\AA}^{-1}$ we measured ~ 800 weak (large $Q_{\perp}$) peaks. This data set has been extended to include the stronger, lower $Q_{\perp}$ peaks using a conventional rotating anode supply and $\text{MoK}\alpha$ radiation for a total of ~ 1100 peaks. Shown below are radial (a) and transverse (b) scans of the 644444 5-fold symmetric peak in which the radial width shows nearly instrumental resolution (the crystal has been ground into a sphere) and the transverse width indicates a mosaic spread of 0.08° .

These data sets are being reduced and a structure determination using various procedures is underway.

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INVESTIGATIONS OF THE CRYSTALLIZATION OF SYNDIOTACTIC POLYPROPYLENE FRACTIONS

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ABSTRACT. The isothermal crystallization of a series of syndiotactic polypropylene fractions (sPP) with constant syndiotacticities and different molecular weights ($\text{MW}=9100$ to 145000) has been studied through differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), and small angle X-ray scattering (SAXS). The equilibrium melting of sPP with about 94% racemic syndiotacticity is $161(\pm 1)^\circ\text{C}$ and the heat of fusion is $8.0(\pm 0.3)\text{ kJ/mol}$ determined from a combination of DSC, WAXD and SAXS measurements. In its most stable form, sPP may form crystals with a mixture of three possible unit cells (I,II,III) with a predominance of either one depending not only on crystallization conditions but also on stereoregularity and molecular weight. The isothermal crystallization as studied by small angle X-ray scattering, employing synchrotron radiation, showed a decrease in the rate of crystallization with increased molecular weight. This change in rate may be an effect of decreased chain mobility and entanglements. The long spacing, L , as determined from the maximum in the Lorentz-corrected SAXS curve appeared to increase with molecular weight for the same supercooling. For any one molecular weight, L was observed to increase with lower supercoolings but during isothermal crystallization of any one fraction, L decreased with crystallization time for a given supercooling. Even though changes in L may reflect changes in crystal thickness there is no simple or direct correlation between the two. In the determination of crystal thickness knowledge of the degree of crystallinity corresponding to an observed long spacing is necessary. A different approach requires the use of a correlation function. Another important issue arises from the lamellar thicknesses range between 2.5 and 5 nm depending on crystallization temperature and molecular weight. The number-averaged syndiotactic block is between 29 and 37 repeat units as inferred from solution nuclear magnetic resonance. In the crystal, $c=0.740\text{ nm}$ consists of four repeat units. As a result, the length of the number-averaged syndiotactic block ranges from 5.4 to 6.8 nm. This may be an indication that no defects should be included in the crystal lattice.

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Observation of diffuse scattering from $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single crystal.

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Local displacements in oxygen atom positions and its changes with temperature were studied in a $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single crystal material. The motion of oxygen atoms associated with tilting of the copper-oxygen octahedra CuO_6 is believed to be crucial in creating and destroying superconductivity. The pair distribution function (PDF) - Fourier transformation of the normalized structure factor of this material - has shown temperature dependence indicating such oxygen motion. Based on PDF analysis we expect to see some changes in the diffuse scattering from a single crystal. Since the amplitude of displacement is small (0.1-0.2 Å) we expect to observe such diffuse scattering at high Q , range 5 - 10 Å.

X-ray single crystal diffraction experiment was carried out with a low background germanium detector in the 10 - 100 K temperature range. High quality single crystals of $\text{La}_{2-x}\text{Sr}_x\text{Cu}$, $x=0.18$ were used.

Anomalous diffuse scattering was around (0,0,14) peak. Instead of simple concentric TDS observed for other peaks we observed unusual depression of TDS along (0,0,1) lines. The intensity of the diffuse scattering changed with temperature. While the overall intensity increases with temperature, the decrease of intensity around (0,0,1) is not so profound at higher temperatures. A sample plot of the scattering intensities for different temperatures was presented in the figure below.

In the follow-up experiment we need to measure the diffuse scattering around (0,0,14) and other peaks with very good statistics in order to describe the changes qualitatively.

NEAR NEIGHBOR DISPLACEMENTS OF ORDERED AND CLUSTERED FeNiCr ALLOYS.

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The FeNiCr alloys contain technologically important and scientifically interesting systems, including invar, permalloy and the stainless steels. Chemical order and atomic size influence the properties of these and other alloys. Anomalous-diffuse scattering measurements at X14 have begun to measure atomic correlations in binary NiFeCr alloys. These measurements will guide efforts to understand the behavior of the FeNiCr and other alloys. With anomalous scattering techniques it is possible to determine like and unlike neighbor distances for different co-ordination shells. An assumption that the unlike neighbor distance is the average of the two like-neighbor distances is not required. The importance of avoiding this so called "hard sphere" model is illustrated in Fig. 1 below. In the $\text{Ni}_{80}\text{Fe}_{20}$ ordering system the Fe-Ni near neighbor distance is found to be shorter than even the Ni-Ni distance.¹ Similarly in the $\text{Fe}_{53}\text{Cr}_{47}$ clustering system the unlike Fe-Cr distance is found to be longer than either of the like distances.² This measurement of a microscopic Vegard's law has stimulated efforts to develop improved theoretical codes which account for chemically sensitive displacements from the average lattice.

Fig. 1a $\text{Ni}_{80}\text{Fe}_{20}$ ordered alloy hard sphere size compared to observed (differences in separations are magnified by 10 for clarity). 1b $\text{Fe}_{53}\text{Cr}_{47}$ clustered alloy showing large unlike neighbor displacements (differences in separations are magnified by 50 for clarity).

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SITE OCCUPATIONS OF Cr ADDITIONS TO ORDERED B2 FeAl ALLOYS

X14A

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Ordered intermetallic alloys with desirable high temperature properties are being studied in an effort to induce practical amounts of room temperature ductility. These normally brittle alloys would have major applications if room-temperature ductility of 2 to 5% could be achieved. Third element additions have been successful in improving ductility in some binary intermetallics. An understanding of which site is occupied by the added third element gives insight to its effect on both properties and phase stability.

Powder diffraction patterns of alloys of near equiatomic Fe Al with ~5 at. % Cr were made with x-ray energies far removed from and 15 eV below the Fe and Cr K edges to effect large contrast changes in x-ray scattering through the anomalous scattering factors. These three powder diffraction patterns at three energies provided a redundant pattern to test for systematic errors in the recovered site occupations. The B2 unit cell is shown in Fig. 1 with the Fe atoms at the corners and the Al atoms at the body centers. As shown in Fig. 2, the number of Al atoms occupying Fe sites is very sensitive to the Al/Fe concentration ratio for alloys containing chromium. As the Al/Fe ratio decreases from $\text{Fe}_{50}\text{Al}_{50}$ (Al/Fe = 1) towards Fe_3Al (Al/Fe = 1/3) the amount of Al on Fe sites increases then takes a sudden drop. This abrupt change in site occupation is most likely related to the approaching phase boundary of Fe_3Al . Chromium atoms predominantly occupy the Al sites for all alloys studied, but had little effect on the mechanical properties. As few studies such as this exist, more systematic efforts are underway so that we can build an understanding about the chemical phase stability of metallic alloys systems.

Fig. 1. The AB unit cell with B2 structure.

Fig. 2. The percent of Fe sites occupied by Al atoms for different Al/Fe ratios. Most all the Cr atoms reside on the Al sites.

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MICRODIFFRACTION MEASUREMENTS OF CORRELATIONS IN GRAIN ORIENTATION IN HIGH CURRENT, HIGH TEMPERATURE SUPERCONDUCTORS

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Polycrystalline $\text{Tl}_1\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ superconducting films are of interest due to their high critical currents, even in strong magnetic fields. X-ray diffraction was used to study grain orientation in an effort to understand both the origin of such high critical currents in a polycrystalline material, and its variability; critical current densities can vary from 2×10^4 to $9 \times 10^4 \text{ A/cm}^2$ over the area of a single film.

Films were grown on polycrystalline yttrium-stabilized zirconia substrates. The grain size was $\sim 3 \mu\text{m}$, with c axes aligned (2° FWHM) normal to the substrate. Diffraction from a 1 cm^2 area shows that the a axes are randomly oriented in the plane of the substrate. Using a $100 \mu\text{m}$ diameter pinhole to illuminate a small area of the film, grain orientations were measured along a $4 \text{ mm} \times 200 \mu\text{m}$ region of the film. The film was patterned so that the conductivity of this region could be measured in 1 mm segments. It was found that within each $100 \mu\text{m}$ region the a axes are locally aligned (10° FWHM). High critical current segments correspond to regions, $\sim 1 \text{ mm}$ in extent, where the in-plane orientation varies continuously. Low critical current regions contain abrupt shifts in orientation.

FIG 1. Orientation and critical current density along a $4 \times 0.5 \text{ (mm)}^2$ region of superconducting film.

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X14A

LATTICE DYNAMICS STUDY OF FCC SOLID ^4He THROUGH X-RAY INTEGRATED INTENSITY MEASUREMENTS

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X-ray study of the high density fcc phase of ^4He yields information regarding the extent to which anharmonic effects are significant with respect to lower density phases, as well as in comparison to Ne and Ar. In a continuing study of the lattice properties of fcc ^4He , the Q and T dependence of x-ray integrated intensities has been measured on a $60.6 \text{ atoms/nm}^{-3}$ sample. The Q-dependent data give a direct measurement of the atomic displacements $\langle u^2 \rangle$ while the T-dependent data done at constant volume give a measurement of $(\partial \langle u^2 \rangle / \partial T)_V$ from which corresponding characteristic temperatures $\Theta_M(T)$ can be obtained for this density.

The sample was grown in situ in a high-pressure Be cell of volume 15 nm^3 mounted on the cold finger of a displux with a minimum attainable temperature of 10 K, which in turn was mounted on a four-circle diffractometer. The cell was pressurized to the melting pressure of 303 MPa using a combination of a compressor plus thermal pressure generation, and then held constant while slowly cooled through the melting temperature of 28.15 K. This resulted in an excellent single crystal sample with a remarkably small FWHM mosaic of 0.23 mrad. For the Q-data we were able to orient the single crystal so as to observe intense ^4He reflections up to (3,3,3) for the first time. Access to higher order reflections was prevented due to geometric restrictions. The measured integrated intensities show the expected $|Q|^2$ dependence after the form factor dependence has been removed. For the T-data, measurements were made on the (2,2,2) reflection in a 10 degree range between the melt and the fcc-hcp transition.

Analysis of the data includes a comparison of the experimentally determined $\langle u^2 \rangle$ with the value obtained from phonon dispersion curves measured with neutron inelastic scattering at the same density. The Q and T data will be correlated with each other and with existing T data previously taken on a rotating anode source at the same density. The two sets of data can also be related through a moments expansion of the $g(v)$ derived from phonon dispersion curves. The comparison also serves as a test for calculated electronic charge densities for ^4He .

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X14A

MAPPING OF RESIDUAL STRESSES OF A CERAMIC-TO-METAL JOINT USING X-RAY DIFFRACTION

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High strength metal-to-ceramic joints are required for advanced automotive engine applications. As would be expected, the large residual stresses resulting from the thermal expansion mismatch make the manufacture of strong joints difficult. These joints are formed with a metal alloy braze layer plus an optional Ti layer. The metal alloy braze (Ti-4.5, Cu-26.7, Ag-68.8 wt.%) is joined to a disc of cast iron and to a disc of ZrO_2 (MgO stabilized). Neutron diffraction mapping has revealed very low tensile residual stresses in the iron portion of the Ti containing structures and much higher residual stresses in the structures without the Ti layer. Additionally, the Ti layer has been shown to increase the shear strength of these joints.

In this study, the residual stresses in zirconia-iron discs, brazed with a metal alloy layer, with and without a Ti transition layer were measured with X-rays as a function of location with respect to the joint. The residual stresses were measured at various key locations indicated by a finite element analysis (FEA) model. The X-ray residual stress mapping results were compared to the neutron diffraction mapping results. These data were combined to provide a complete residual stress profile of these samples and were compared with the FEA model.

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RESIDUAL STRESS DISTRIBUTION IN GRADED CERAMIC-TO-METAL JOINTS

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Gradient materials have been proposed for mitigating interface mismatch stresses; however, a fundamental understanding of stresses and stress reduction mechanisms in these materials is lacking. This research is aimed at understanding the effects of specimen geometry and microstructure on the residual stress distribution in graded ceramic-to-metal joints. Model materials systems and simple specimen geometries are being studied. Experimental measurements of residual stresses will be carried out using X-ray diffraction, and the results will be compared with those obtained by FEM modeling.

Graded Al_2O_3 -Ni specimens will be produced at the INEL using powder metallurgy techniques. The fabrication process involves hot isostatic pressing of layered green compacts. A rod-shaped specimen, 12 mm in diameter by 25 mm in length, will be examined. Modeling results indicated significant differences in the overall residual stress distribution for this specimen. Interlayer thicknesses of 3 mm will be studied, and the volume fraction will vary either linearly or in a non-linear fashion described by a power law expression. This specimen was selected based on modeling results. Surface volume averaged residual strains will be measured experimentally using the well known " $\sin^2\Psi$ method." It is desirable to use an X-ray spot size as small as practicable; e.g., 1 mm interlayers will be evaluated. Residual stresses in the composite interlayers will be evaluated.

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Arsenic Dimers on Si(100): An X-Ray Standing Wave Perspective

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We used the X-ray standing-wave technique to measure the position of As atoms on the As-terminated Si(001)-(2x1) surface. Arsenic was deposited onto a clean Si(001)-(2x1) surface which was held at temperatures between 400°C to 700°C. Figure 1 shows the (400) and (220) reflections as open squares and the corresponding As K α normalized fluorescence yields as open circles. The solid lines are calculated from dynamical diffraction theory and fitted to the data. We extracted, from these fits for the two reflections, the coherent position, P, and coherent fraction, F, of the As atoms. From an analysis of the data we determined that the dimers are symmetric (buckling angle < 2°), the bond length of the arsenic dimers is 2.58 ± 0.04 Å, and the mean position of the dimers lie almost directly on the projected bulk Si lattice planes, indicating nominal surface relaxation. These results compare well with theoretical predictions and other experimental conclusions.

We also measured the coherent position and fraction of the As dimers as a function of temperature. Figure 2 shows a plot of the mean-squared vibration amplitude of the As dimer as a function of temperature for the (400) reflection. The solid line is a polynomial fit to the data and the coefficients of the fit are indicated in the inset box. Up to 700K $\langle u^2 \rangle$ varies linearly with temperature and this is reasonably consistent with theory, indicating the As atoms are vibrating within the normal harmonic approximation of the Debye model. However, we find that above 700K this approximation breaks down and the As dimers vibrate with a significant amount of anharmonic behavior; this has yet to be verified theoretically.

Figure 1

Figure 2

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The Behavior of Bismuth Dimers on Si(100)

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The adsorption of As on Si(100) forms a 1 ML ideal passivated surface composed of symmetric As dimers in a nominal (2x1) reconstruction. Bi, however, probably due to its 25% larger covalent radii, forms (2xn) irreversible phase transitions as a function of substrate temperature during deposition, where $13 > n > 5$ for $200^\circ\text{C} < T_{\text{sub}} < 550^\circ\text{C}$. We used the x-ray standing-wave (XSW) technique to study the evolution of these Bi dimers as a function of coverage and substrate temperature, T_{sub} .

Figure 1 shows the XSW measurements for the saturated Bi surface produced by evaporating Bi onto a Si surface held at 400°C followed by a 15-minute anneal at 500°C . The LEED pattern showed weak two-domain 1/2-order spots with weak 1/5-order streaks and a high background. Comparing this to the As/Si(100) LEED pattern, which showed sharp 1/2-order spots with a low background, the Bi XSW results were surprisingly similar to the As XSW results (see the As/Si(100) abstract). The high F_{400} indicates that the Bi dimers do not reduce their strain by buckling. From these two reflections we determined that the dimer bond length was $3.01 \pm 0.04 \text{ \AA}$ and the center-of-mass of the dimer sits 27% above the bulk-extrapolated (400) planes. These distances correspond to an expected 25% increase from the As/Si(100) case.

Figure 2 shows the (400) coherent position and fraction for a few coverages at both $T_{\text{sub}} = 500^\circ\text{C}$ and $T_{\text{sub}} = 250^\circ\text{C}$. The relative constancy of the P_{400} and F_{400} values at 500°C attests to the stability of this phase as a function of coverage. One preliminary interpretation of the low-temperature (metastable) data suggests that the Bi_4 molecule does not completely dissociate upon striking the Si surface. And only when the density of Bi_4 molecules becomes sufficiently large could the dimer ordering be induced.

Figure 1

Figure 2

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X-ray Standing Wave Structural Study of the Dimerized Ga/Si(100) Surface

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In the case of Ga adsorbed on the Si(100) surface, a dimer model (Fig. 1) was proposed by Bourguignon *et al.* based on LEED and AES studies. This model has been verified by recent STM results. In our studies, we have precisely measured the Ga dimer lengths and the dimer heights relative to the Si lattice structure using X-ray standing waves (XSW). The Si sample was polished and chemically etched before insertion into the UHV chamber. Ga was deposited at room temperature at coverages of 0.3, 0.4, 0.5 and 1.0 ML. The Si reflectivity and Ga K α fluorescence were measured for both (400) and (220) Bragg reflections as a function of incident angle θ . By fitting the rocking curve and fluorescence yield to dynamical diffraction theory, we determined the coherent fraction (f) and the coherent position (p) for the Ga distribution. (See Table 1.) We then calculated the Ga-Ga dimer bond length (ℓ) and the height (h) of the Ga dimer relative to the Si (400) diffraction plane. Results listed in Table 2 and illustrated in Fig. 1 suggests that the structure of the Ga dimer are independent of the Ga coverages (θ). According to the Bourguignon model, Ga dimers are forming on top of the dimerized Si 2x1 surface at $\theta \leq 1/2$ ML and above $1/2$ ML, Si dimers are broken. However, our results do not show any evidence of this phase transition. It is also shown in our result that the Ga ordered fraction is strongly dependent on Ga coverage showing a significant decrease above $\theta = 1/2$ ML. This indicates that at higher coverages Ga atoms are forming randomly distributed clusters on the Si surface. The fact that the total amount of ordered Ga atoms saturates at 0.5 ML means one can only grow a smooth Ga layer on Si(100) surface up to $1/2$ ML. We also found that annealing the surface to 350°C produced an irreversible phase transition which reduced the coherent fraction dramatically. This provides the evidence that some Ga dimers were broken during the annealing and formed clusters permanently. In conclusion, we found that Ga is likely to form clusters instead of dimers at coverages above $1/2$ ML and at elevated temperatures. This is in strong contrast to the more stable As/Si(100) surface.

Table 1 Coherent fraction and coherent position

θ	0.3 ML		0.4 ML		0.5 ML		1.0 ML	
Ref.	(400)	(220)	(400)	(220)	(400)	(220)	(400)	(220)
f	0.73 ± 0.01		0.68 ± 0.01	0.34 ± 0.01	0.67 ± 0.01		0.43 ± 0.01	0.23 ± 0.01
p	0.76 ± 0.01		0.75 ± 0.01	0.84 ± 0.01	0.75 ± 0.01		0.77 ± 0.01	0.87 ± 0.01

Table 2

θ (ML)	Ord. frac.	ℓ ($\text{\AA}$)	h ($\text{\AA}$)
0.3	85%		1.03 ± 0.01
0.4	80%	2.48 ± 0.04	1.02 ± 0.01
0.5	78%		1.02 ± 0.01
1.0	50%	2.51 ± 0.06	1.04 ± 0.01

Fig. 1

Research supported by U.S. DOE BES material science contract No. W-31-109-ENG-38.

**Structural Determination of the Si(111) $\sqrt{3}\times\sqrt{3}$ -Bi Surface
by the X-ray Standing Wave Technique**

J.C. Woicik (NIST), G.E. Franklin (Harvard), J.R. Patel (AT&T),

M. Bedzyk (Northwestern), and J.A. Golovchenko (Harvard).

X-ray standing wave measurements utilizing [111], [11-1], and [220] diffracting planes determine the honeycomb phase of the Si(111) $\sqrt{3}\times\sqrt{3}$ -Bi surface to consist of 2/3 monolayers of Bi atoms, each located directly above a first layer Si atom with no lateral reconstruction. The [111] position, 0.97 [111] lattice units, places the Bi layer 2.68 Å above the first layer Si atoms, corresponding to a Bi-Si bond length equivalent to the sum of the Bi and Si covalent radii. This geometry explains the strong voltage dependence of recently reported tunneling images [Shioda et al., *Phys. Rev. B*, **48**, 4895 (1993)].

**X-RAY STANDING WAVE ANALYSIS OF TWO DISCOMMENSURATE
PHASES OF Ga ON Ge(111)**

J. Zegenhagen (Max-Planck-Inst., Stuttgart, Germany), G. Franklin (Harvard Univ.)

The whole phase diagram of Ge(111)/Ga exhibits surprisingly no stable, commensurate surface structure. Yet, in the coverage range 0.2 ML – 2 ML Ga introduces several discommensurate phases on the Ge(111) surface. This means the surface structure is within domains almost commensurate, i.e. exhibits a moderate mismatch. These domains are separated by regions (discommensurations = light or heavy walls) where the adsorbate loses phase coherence with the substrate. We characterized two of these phases with saturation coverages of about 0.7 ML and 0.8 ML, respectively, by x-ray standing waves (XSW) employing (111) and (11 $\bar{1}$) reflections. The results are shown in Fig. 1. For the preparation with lower coverage the analysis reveals that Ga occupies exactly the substitutional position in the top Ge(111) double layer but, as the low $F^{11\bar{1}}$ value shows with a significant lateral distribution around this mean position consistent with about +7% lattice mismatch in the interior of the domains. For the other preparation (0.8 ML) the vertical position (P^{111}) of Ga is unchanged. However $P^{11\bar{1}}$ has shifted significantly and $F^{11\bar{1}}$ is drastically decreased. These results can be understood if about half of the Ga occupies now substitutional sites in surface regions which exhibit a stacking fault.

Fig. 1 XSW (111) and (11 $\bar{1}$) results for annealed Ge(111)/Ga. $E_\gamma = 10.4$ keV. Left: 0.7 ML. $P^{111} = 0.95$, $F^{111} = 0.95$, $P^{11\bar{1}} = 0.83$, $F^{11\bar{1}} = 0.48$. Right: about 0.8 ML, $P^{111} = 0.95$, $F^{111} = 0.87$, $P^{11\bar{1}} = 0.74$, $F^{11\bar{1}} = 0.13$. Symbols are data and solid lines fits to the data.

X15B

TOP SITE ADSORPTION FOR K ON Cu(111) AND Ni(111) DETERMINED BY SEXAFS

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Alkali metals adsorption on metal surfaces has received much attention recently because alkali atoms have been observed to adsorb on top of substrate atoms rather than in hollow sites. That this result runs counter to that of *any* known adsorbate on a metal surface is significant, but that it occurs for an alkali — one of the oldest studied and 'simplest' adsorbates — demands that conventional wisdom and perceived understanding of alkali-atom bonding should, at the least, be re-evaluated.

We have used surface extended x-ray absorption fine structure (SEXAFS) measurements from p(2x2) overlayers of K on Ni(111) and Cu(111) surfaces and find that at 65 - 70 K potassium occupies the atop site on both substrates, with bond lengths of 2.92 ± 0.02 Å on Ni and 3.05 ± 0.02 Å on Cu (see Figs. 1 and 2). The identical adsorption site and small change in bond length are consistent with the expected dominance of adatom-adatom interactions in these near-saturation metallic adlayers. The inability to obtain SEXAFS data from K at lower coverages on these surfaces and at these temperatures, indicative of disorder/multi-site occupation, is further evidence of a relatively weak alkali-substrate interaction even in the dilute-adatom, non-metallic-overlayer regime. Based on these and a variety of structural results in other systems, we conclude that a delicate balance of coverage, substrate corrugation, and adatom size is required for atop adsorption to occur. We also conclude that there presently exists *no* definitive evidence for a change in alkali-adatom bond length in going from the low- to high-coverage regime.

Fig. 1. Background-subtracted, edge-normalized, k^2 -multiplied SEXAFS data for K/Cu(111) at grazing and normal incidence. Absence of first-shell SEXAFS at $k > 4$ Å⁻¹ in normal incidence immediately identifies atop adsorption site. SEXAFS < 4 Å⁻¹ is mainly due to second shell. Result of two-shell fit, similar to that in Fig. 2, is also shown.

Fig. 2. Top: Comparison of K/Ni(111) filtered SEXAFS data with results of a two-shell least-squares fit. Filtered data obtained from Fourier transform of grazing-incidence data, similar to that shown at top in Fig. 1. Bottom: Individual first- and second-shell contributions to fit in top panel. Note significantly shifted amplitude function of second shell due to enhanced in-plane vibrational motions.

IDENTIFICATION OF SI OCCUPYING AS vs GA SITES IN SI-DOPED GaAs USING NEXAFS

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 AT&T Bell Labs

One of the most common dopant-semiconductor systems, Si in GaAs, is also one of the most difficult to characterize structurally for several reasons. (1) Amphoteric Si usually occupies both Ga and As sites. Separate model systems, with only Ga or As sites being occupied and with Si concentrations of $\sim 10^{16}$ cm⁻³ (30 ppm), are required. So far, only a model with Si in Ga sites has been available. (2) Even with both models, it is difficult to distinguish between the two sites using EXAFS because Si-As and Si-Ga bond lengths, as well as As and Ga backscattering amplitudes, are so similar. (3) The Si K edge at 1.84 keV requires monochromating InSb(111) crystals, whose poor thermal conductivity leads to output-beam instabilities due to unavoidable heat-load variations; this problem is particularly significant in low-concentration systems. (4) The fluorescent background from GaAs is not only very large, but is close in energy to the low-intensity Si signal.

We report NEXAFS data which overcome all of these difficulties. Heat-sunk InSb(111) crystals located downstream from a harmonic-rejecting mirror, coupled with our beam-position feedback system, provide an extremely reproducible output beam. The focusing mirror is downstream from the monochromator, maintaining the natural energy resolution from the crystals and beam size. The ~ 220 -eV resolution of the multi-element Ge detector helps discriminate the Si K α signal at 1.74 keV from the dominant Ga and As L α background centered at ~ 1.2 keV. A Be foil placed between the sample and detector attenuates the lower-energy background. Finally, we use a low-Si-doped GaAs(311)A sample, an ideal model because only As sites are occupied. Figs. 1 and 2 illustrate the success of this approach and the following abstract describes how it is applied.

Fig. 1. Measuring Si K α fluorescence from dilute Si-doped GaAs. Upper: No Be filter, showing dominant background from GaAs host. Middle: With Be filter. Note scale factor and greater attenuation of Ga L α fluorescence. Lower: Difference between spectra taken with Be filter just above and just below Si K edge, revealing Si K α signal. Taking 0.17- μ m effective sampling depth into account (this includes geometric factors), sample shown reflects 2.5×10^{13} Si atoms cm⁻², or 1/30th of a Si monolayer.

Fig. 2. Si K-edge NEXAFS data for Si in different environments. All data normalized to common edge jump, indicated by unit tick mark on ordinate. Si_{Ga} = Si in Ga sites, bonded to As, from low-concentration Si in GaAs(100); Si_{Si} = Si in Si sites, bonded to Si, from low-concentration Si in GaAs(311)A; Si_{Ge} = Si in Ge sites, bonded to Ge, from 3% Si in Ge. Note that absorption edge shifts monotonically towards higher energy with increasing transfer of charge from Si to its nearest neighbors, as expected.

INADEQUACY OF AUTOCOMPENSATION TO ACCOUNT FOR THE ELECTRICAL DEACTIVATION IN HIGHLY SI-DOPED GaAs

S. Schuppler, D. L. Adler, L. N. Pfeiffer, K. W. West, E. E. Chaban, and P. H. Citrin
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Low concentrations of Si grown on GaAs(100) occupy substitutional Ga (*n*-type) sites, but at higher doping levels the Si atoms begin to occupy As (*p*-type) sites as well. Thus, the free-carrier electrons from the donor Si atoms become trapped by the acceptor Si atoms, making the sample electrically less active. Despite the general acceptance of this autocompensation mechanism, no experimental evidence exists for quantifying its importance. Using Si *K*-edge NEXAFS data, we report the first experimental determination of Si atom concentrations occupying As sites in Si-doped GaAs(100). The data directly show that autocompensation, though present, is clearly insufficient to explain the observed large reduction of free carriers. The results, see figures and captions, thus indicate that other deactivation mechanisms are much more significant than previously believed. Work is in progress to identify the additional mechanism(s).

Fig. 2. Determining upper-limit $[Si_{As}]$ in VH-(100) sample. Assuming Si occupies only As and Ga sites, represented by L-(311)A and L-(100) data, VH data (bold line) are fitted between 1834-1839.3 eV. Result (labelled "Sum") gives fractional $[Si_{As}] = 29\%$. Note misfit with data between 1839.3-1845 eV, showing Si must be present in other than As and Ga sites. Additionally, using 29% value, a lower-limit electrical activity of 42% $[100\% - 2 \times (29\%)]$ is predicted, whereas an even lower 7% activity is measured, again showing need for invoking different Si sites. Insert: Normalized (100) data, making $[Si_{As}]$ more apparent.

Fig. 1. Si *K*-edge NEXAFS from (100)- and (311)A-oriented GaAs vs Si concentration, labelled low (L), medium (M), high (H), and very high (VH). Edge jumps normalized to VH-(100) data, whose $[Si] = 4.9 \times 10^{19} \text{ cm}^{-3}$ (note scale factors). Peak absorption position for Si in As and Ga site indicated by vertical lines. Note that as $[Si]$ increases, occupation of Si in opposite sites for both samples also increases.

LOCAL STRUCTURE OF LUMINESCENT POROUS SILICON

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The potential utility of room-temperature luminescence from anodically-grown porous silicon (por-Si) has generated intense interest, and several mechanisms have been proposed to explain its origin. Of those mechanisms — quantum-confined structures, amorphous Si, surface SiH_x , and siloxene — only the first two remain viable candidates (our work last year ruled out siloxene, while luminescence from por-Si passivated with O rather than H has ruled out SiH_x). Despite a growing consensus for quantum confinement, there is still debate about the dimensions, shape, and crystallinity of the structures believed responsible for the optical activity. This is largely due to the lack of structural information within the penetration depth of the photoexciting radiation. For typical 80%-porosity samples with peak luminescence from ~350-400-nm exciting light, this depth is only 500-1000 Å, which is not well suited for study with either TEM or STM. Furthermore, structures smaller than ~20 Å, should they be significant, are beyond practical detection with diffraction.

We have obtained Si *K*-edge total-electron yield EXAFS measurements which place new and unexpectedly lower constraints on the macroscopically-averaged size of particles contained within the relevant depth of 500-1000 Å. This is directly determined from EXAFS amplitudes (see figure and caption): since H negligibly backscatters, the reduced coordination in por-Si leads to an average H:Si ratio, and this leads to an effective surface/volume ratio for the average Si particle. Our results, which indicate H:Si values almost ten times larger than the most concentrated a-Si:H samples known, clearly rule out the wire-like structures presently believed to be important in por-Si. These large H:Si values were independently confirmed by α -recoil measurements.

Fig. 1. Top: Fourier-transformed Si *K*-edge EXAFS data taken at 77 K from c-Si, a-Si, and two differently-prepared por-Si samples with comparable quantum efficiencies. Note reduced but measurable crystalline nature of por-Si samples as seen in their 2nd- and 3rd-shell structures at ~3.4 and 4.1 Å (uncorrected for phase shift). Peaks at ~2.5 and 2.9 Å are artifactual.

Bottom: Filtered 1st-shell data from top panel. Note amplitude function is shifted only for a-Si as a result of static disorder, while amplitude function for por-Si samples is unshifted, indicating reduced effective coordination due to H at surface. Average H:Si in por-Si (B) sample is 1.0 ± 0.1 , implying $100 \pm 10\%$ H, or a surface/volume ratio ~3 times larger than previously believed for 20-30 Å particles. Such a result also rules out presently proposed wire-like structures, whose surface/volume ratios are much too small.

GLANCING ANGLE X-RAY SCATTERING STUDY OF THE SURFACE MELTING MECHANISM ON AL(111) SURFACES

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The surface melting phenomenon in fcc metals, like Pb and Al, has been studied in the past by various surface techniques. While all experiments performed so far on Pb(110) and Al(110) agree that well below the bulk melting point a surface disordering process takes place, the detailed nature of this fundamental surface phenomenon is still rather unclear. Glancing angle X-ray scattering should be ideally apt to attack this problem.

In a first two weeks experiment we measured the temperature dependence of some selected crystal truncation rods, of glancing angle Bragg scattering and of glancing angle diffuse scattering at the Al(110) surface ($T_m = 933.5$ K). By way of example we show in Fig. 1 the transverse profile of the (LL1)-rod at $L=0.99$ at 592 K, 779 K and 886 K. The temperature dependence of this intensity distribution indicates a severe disordering of the surface between 780 K and 860 K, however, most interestingly, the surface dominated diffuse scattering around the (002) reflection shows no indication of a surface anomaly. The $(\bar{1}11)$ Bragg intensity displayed a decrease around 860 K (Fig. 2) whose characteristics are being studied at the moment by analysing the measured α_f -profiles. Furthermore, we looked for diffuse scattering associated with a quasiliq, which is expected to be located on diffuse scattering rings around each Bragg point. At 870 K, we found diffuse intensity clearly above background around (000) which exhibits a large coherence length in the radial direction and remains almost constant within an angular interval of $\pm 10^\circ$ around a high-symmetry direction. We are currently analysing whether this finding can be related to the surface melting phenomenon.

Fig. 1: Transverse profiles of (LL1)-rod at $L=0.99$ before and after roughening transition

Fig. 2: α_f -integrated intensities of $(-1\ 1\ 1)$ -reflection for various incidence angles α_f

Surface Segregation Above T_c in Cu_3Au (001)

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Alloys of copper and gold have been the subject of diverse study spanning a range of topics in physics and material science such as phase transitions and dislocations, respectively. A great deal of theoretical discussion has focused on the influence of a system's dimensionality on an order-disorder phase transition. Cu_3Au is one of the best known and most widely studied binary alloys. With the recent development of lower dimensional x-ray scattering techniques, Cu_3Au has been revisited in an attempt to shed some light on the problem of dimensionality. Ordering in the near surface region (at depths on the order of the alloy's correlation length) can be greatly affected by the nearby surface. Through crystal truncation rod (CTR) analysis of Cu_3Au (001), we have made the exciting discovery of surface segregation in approximately the top ten layers, at temperatures well above T_c . It has been reported in other measurements that above T_c ($\approx 384^\circ\text{C}$ for our sample,) Cu_3Au (001) terminates with a top layer composition of 50 % Cu and 50 % Au. With our measurements, we find that not only is there surface segregation, but exists an exponentially decaying oscillatory surface segregation, a number layers into the surface.

In the figure below, the (20L) (using FCC indexing) CTR is plotted for two temperatures above T_c where the solid lines are fits to the data. Above T_c , for bulk Cu_3Au (001), each layer can be replaced by an average composition of 3:1, Cu : Au. The model we use to fit the CTRs consists of a layer-wise

scattering factor F_L that depends on the individual scattering factor of Cu and Au and is weighted by their layer concentration with $F_L = 1$ for a 3:1 ratio. In the ordered state, the crystal is made up of alternating layers of 1:1 and 1:0, Cu : Au, and a (201) Bragg peak exists. For a perfectly disordered crystal, $F_L = 1$ for all layers and for the ordered state it would oscillate between its 1:1 and 1:0 value without decaying. We observe that above T_c the broad peak at $L = 1$ fits well to an oscillating but exponentially dampened layer scattering factor model that decays more rapidly at higher temperature. The inserts to the figure show the layer scattering factor vs. layer number into the bulk for the two fits. From these histograms we see the oscillations, showing segregation, die away faster at 520°C (136°C above T_c) than at 386°C (2°C above T_c). We conclude from these fits that Cu_3Au (001) above T_c shows, exponentially decaying temperature dependent, oscillatory surface segregation.

INITIAL STAGES IN THE EPITAXIAL GROWTH OF NaCl ON Ge(001)

C. A. Lucas, G. C. L. Wong (Lawrence Berkeley Laboratory), C. S. Dower (U. of Edinburgh, U.K.), F. J. Lamelas and P. H. Fuoss (AT&T Bell Laboratories).

We have performed an *in-situ* x-ray scattering study of the initial stages of NaCl/Ge(001) heteroepitaxy. The $c(4 \times 2)$ surface reconstruction, characteristic of Ge(001) at low temperature, is suppressed immediately upon deposition of NaCl. However, the (2×1) symmetry of the surface unit cell is preserved, even after six monolayers of NaCl have been grown. Analysis of the in-plane, half integer Bragg reflections, specific to the (2×1) reconstruction, supports a model in which the Ge dimer remains and sodium is adsorbed into the "valley" site (in rows between the dimers).

Specular reflectivity measurements were performed during interruptions of the NaCl deposition to gain insight into the growth mode on the modified surface. The results are shown in the figure for (a) the clean Ge surface and after (b) 20 seconds, (c) 60 seconds and (d) 120 seconds of NaCl deposition at a substrate temperature of 180K. Data in (e) was taken after the sample had been annealed at 470K for approximately 5 minutes. All measurements were performed at room temperature. The solid lines are fits to the data in a simple two-layer model, i.e. film + substrate. The most striking result is that the thickness of the layer is constant ($\sim 8.3 \text{ \AA}$) as the growth proceeds (evidenced by the single oscillation period in the data). This corresponds to growth as islands, three monolayers high, which fill in until a pseudomorphic film is obtained. Annealing of the film causes the islands to increase in height but does not disrupt the Ge-Na (2×1) surface.

Growth via triple-layer high islands, on a surface modified by dissociative chemisorption of the arriving molecules, is very similar to the growth mechanism observed in $\text{CaF}_2/\text{Si}(111)$ heteroepitaxy, another example of an ionic/covalent system.

Reference. C. A. Lucas et al. Surface Science, **286**, 46-55 (1993).

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ORDER-DISORDER $C(4 \times 2)$ - (2×1) TRANSITION ON Ge(001)

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Using *in-situ* x-ray diffraction, we have investigated the order-disorder transition on the Ge(001) surface by measuring the temperature dependence of the $(1.75, 0.5)$ reflection, specific to the $c(4 \times 2)$ low temperature phase. Figure 1 shows the temperature dependence of the measured HWHM's obtained from Lorentzian lineshape fits to the data for scans along the $[0 1]$ and $[1 0]$ crystallographic directions. The dashed lines are guides to the eye and indicate the different saturation temperatures. The fact that the domain sizes (related to the inverse of the peak widths) have saturated implies that the antiphase domain boundaries are being pinned, probably by defects or impurities. Figure 2 shows the temperature dependence of the inverse peak intensity, $1/I_p$, of the $(1.75, 0.5)$ reflection.

Fig. 1

Fig. 2

In order to compare our results with the 2D Ising model, we note that the $c(4 \times 2)$ - (2×1) transition is equivalent to that of an order-disorder transition in an AB alloy, which can be described by a spin variable which represents the occupation or dimer orientation at a particular site. The structure factors of the two dimer orientations simply replace the coherent scattering lengths in the alloy. The results indicate that the transition corresponds to a 2D phase transition with anisotropic interaction energies along and perpendicular to the dimer rows. Due to pinning of the $c(4 \times 2)$ domains we are unable to observe any universal critical behavior. Our scattering model is qualitatively capable of reproducing the intensity distribution of the measured $c(4 \times 2)$ superlattice reflections. The model is consistent with the presence of asymmetric dimers on the surface. At low temperatures the dimers order into $c(4 \times 2)$ domains separated by antiphase domain boundaries which correspond to local $p(2 \times 2)$ ordering. As the temperature is increased the domain sizes decrease but the number of buckled dimers is conserved. This implies that the (2×1) phase at higher temperatures consists of a random array of buckled dimers.

Reference. C. A. Lucas et al. Physical Review B, **47**, 10375-10382 (1993).

Work supported by U. S. Department of Energy under contract No. AC03-76SF00981

X16A

Anomalous coverage behavior of the Cs-Ag distance on Cs/Ag(110)

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Cs induces a (1x2) missing-row reconstruction on the Ag(110) surface. We determined this structure by X-ray diffraction for two different Cs coverages: 0.2 and 0.3 monolayers.

Our determination reveals the missing-row reconstruction with every other densely packed [110] Ag row removed and with the Cs occupying the resulting troughs. Annealing this system (150°C to 200°C) leads to a well-ordered structure.

The figure shows the (1/2,0,L) and the (3/2,0,L) superstructure rods of diffraction, measured for two different Cs coverages ($\theta \approx 0.2$ and $\theta \approx 0.3$) and the corresponding fits of a model to the data. The model includes relaxations of four layers of the (1x2) Ag(110) substrate and needs a random mixture of two kinds of Cs atoms, both adsorbed in the troughs of the missing-row: The first kind corresponds to Cs atoms adsorbed in (high symmetry) hollow sites with respect to the second Ag-layer. The second one simulates a floating, incommensurate chain of Cs atoms along the [110] direction.

The shift of the position of the maximum of the (1/2,0,L) rod towards higher L with increasing Cs coverage shows directly the main result of this study. This position is mainly determined by the average interlayer distance between Cs and the first Ag-layer, so our data reflect directly a decrease of the average Cs-Ag layer distance with increasing Cs coverage.

Furthermore we found that at low Cs coverage a large fraction of the Cs atoms assume the high symmetry adsorption sites with fewer in the incommensurate chain. This leads to the Cs contributions to the (1/2,1,L) rod, which show up as a small hump in the figure. The position of this hump is determined by the Cs-Ag layer distance of the Cs in the fourfold hollow site, which is found to be considerably higher than the Cs in the incommensurate chains. At high coverage on the other hand all Cs is found in the incommensurate chains.

Our discovery of a decrease of the average Cs-Ag layer distance with increasing Cs-coverage is anomalous. Previous theoretical and experimental work for alkali adsorption on unreconstructed metal surfaces has shown that increased Cs coverage leads to a more metallic adsorbate-substrate bond, increasing the Cs-Ag distance. This discrepancy can be solved, considering a phase separation between Cs in the incommensurate chain and hollowsite Cs with higher adsorption sites. Cs-substrate interactions at low coverage force part of the Cs into high symmetry adsorption sites, whereas at high coverage the Cs-Cs interaction is dominating, disregarding the substrate and thus leading to an incommensurate chain. Upon closer inspection one finds that the high adsorption height of the Cs actually maximizes its coordination since the top layer Ag atoms have comparable distances to the Cs as the second Ag-layer. Hence our result points to a transition from a system, which is dominated by the Cs-Ag bonding, towards a system, where the adsorbate structure is determined by the Cs-Cs interaction, with increasing coverage.

X16A

"X-Ray Diffraction Study of the Si(111)-($\sqrt{3}\times\sqrt{3}$)Pd Surface"

P. Yang, M. Lee, P. Bennett, (Physics - ASU.), P. Eng and I. K. Robinson (U. of Illinois)

We have studied the atomic structure of the Si(111)-($\sqrt{3}\times\sqrt{3}$)Pd surface using X-ray diffraction. Fig. 1 shows a set of raw "in-plane" data in a 120 degree sector and for Q_{par} values out to $4G_s$ where G_s is the silicon surface unit vector. This data will be compared with model calculations from which one can determine the z-projected unit cell structure. Fig. 2 shows "out of plane" data in the form of a rod scan for the (1,0) $\sqrt{3}$ superlattice rod.

Here, $L=3$ corresponds to the silicon bilayer spacing of 3.13Å. These data show that the $\sqrt{3}$ structure contains appreciable vertical structure. From the $\pm L$ symmetry of this curve, it is apparent that the structure has 6-fold symmetry. This curve will be matched with rod calculations holding the in-plane structure parameters fixed.

These studies are part of our program (PAB) to study the initial stages of epitaxial growth in silicides. The Pd $\sqrt{3}$ surface is particularly interesting because of its possible close relation to the highly controversial Ag $\sqrt{3}$ structure.

Furthermore, this is a highly reactive, epitaxy forming system, with thicker layers forming epitaxial Pd₂Si with a $\sqrt{3}$ coincidence lattice. We plan to explore the transition from monolayer to multilayer structure in future studies, with parallel efforts at ASU using Auger, STM and LEEM.

Work supported in part (PAB) by NSF #DMR9221201.

DIFFUSE X-RAY SCATTERING STUDIES OF HEAVY FERMION SYSTEMS

M. Aronson, R. Clarke, C. Taylor (U. Michigan), R. MacHarrie (AT&T Bell Labs)

Recently, there is mounting evidence that the magnetic ordering of rare earth and actinide based "heavy fermion" intermetallics is strongly affected by microstructural variations, and indeed in some cases may even be an extrinsic effect. For example, as-grown URu_2Si_2 orders antiferromagnetically at 17.5 K with an ordered moment of $\sim 0.03 \mu_B$. In some high quality single crystals, ferromagnetism with an onset temperature of 35 K develops after aging for several weeks, suggesting a central role for microstructural imperfections, perhaps induced by an unusually high susceptibility to intrinsic radiation damage. We have studied one such crystal of tetragonal URu_2Si_2 displaying ferromagnetism and find that the structural coherence is unaffected, having a correlation length of $\sim 1000 \text{ \AA}$ in the ab plane, and exceeding $3000 \text{ \AA}$ in the c direction, similar to that reported in single crystals without ferromagnetism. We conclude that the origin of the ferromagnetism in URu_2Si_2 cannot be stacking disorder, but more likely results from compositional disorder affecting the Ru and Si sites.

A similar sensitivity to microstructure has been documented in hexagonal UPt_3 . Some, but not all, as-grown samples display antiferromagnetic order at 5 K, while others develop antiferromagnetism on aging. While ordered stacking faults have been directly imaged using Transmission Electron Microscopy and a model proposed to link their density to the ordered moment in UPt_3 , the connection of the stacking faults to the initial growth conditions is unknown. We examined a series of UPt_3 polycrystals subjected to varying high temperature annealing schedules. We find that annealing has a dramatic effect on the degree of crystalline order present in UPt_3 , in some cases reducing linewidths by several orders of magnitude.

REAL-TIME X-RAY SCATTERING STUDIES OF Ge (110) OVERLAYERS ON GaAs (110)

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We have studied the annealing of Ge overlayers grown on lattice-matched GaAs (110) substrates by Molecular Beam Epitaxy. The growth temperature, $250\text{--}420^\circ\text{C}$, was deliberately chosen to be well below that required for long range coherent epitaxial growth. The resulting overlayers are nevertheless epitaxial (with in-plane crystallographic alignment) but the grain size is limited to approximately $100 \text{ \AA}$. This type of low-temperature MBE-grown system is of interest for ultrafast photo-detectors in the sub-picosecond regime.

X-ray angular dispersive techniques are used to monitor the perpendicular lattice spacing in the overlayers as a function of time at various annealing temperatures up to 600°C . The Lemonnier-type curved-crystal monochromator at beam line X16-B is ideal for this purpose [1].

The results obtained to date show clear evidence for dramatic increases in the coherence of the overlayer at annealing temperature above 550°C . The measurements correlate well with in-situ RHEED data, taken during growth, which probe the epitaxial structures in the plane of the overlayers.

1. R. Clarke, W. Dos Passos, W. Lowe, B. G. Rodricks, and C. Brizard, Phys Rev. Let 66, 317 (1991)

Optics for Inelastic X-ray Scattering*

X16B

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Monochromator and analyzer crystals intended for inelastic x-ray scattering spectroscopy with the CHSS-APS undulator¹ were tested on the bending magnet. A Si(620) channel-cut monochromator was placed after the primary monochromator, and the two monochromators were scanned in tandem. The (620) reflection was asymmetric with an asymmetry angle of 59° to broaden the acceptance to 35 microrad. A Ge(444) analyzer was used in back reflection at a fixed energy of 7.59 keV. The analyzer was constructed by waxing 3 mm Ge cubes onto a spherically concave glass surface having a radius of 1 m. The cubes covered a roughly circular area having a diameter of 80 mm. The analyzer was positioned at a Bragg angle of 89.14° .

The overall resolution of this arrangement was limited by the divergence from the bending magnet. As shown in the figure, we measured 0.65 ± 0.03 eV for the width of the elastic peak scattered from Be at a scattering angle of 30° .

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¹ D.H. Bilderback, B.W. Batterman, M.J. Bedzyk, K. Finkelstein, C. Henderson, A. Merlini, W. Schildkamp, Q. Shen, J. White, E.B. Blum, P.J. Viccaro, D.M. Mills, S. Kim, G.K. Shenoy, K.E. Robinson, F.E. James, and J.M. Slater, Rev. Sci. Instrum. **60**, 1419 (1989).

X16B

Etching of the Si(100) Surface

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Wet etching of Si surfaces is an important step in the preparation of silicon wafers in the production of integrated circuits. The wafers as grown are usually sealed with a thin oxide film that has to be removed before further processing. The aim is here to conserve or even improve the roughness of the Si interface. We have developed a chemical flow cell that can be mounted on a standard 4-circle diffractometer and allows an *in-situ* observation of the etching process. Si(100) samples have been etched with aqueous HF and buffered $\text{NH}_4\text{F}/\text{HF}$ solutions at pH values ranging from 2 to 8. HF removes the surface oxide rapidly, but etches the Si substrate very slowly. Surface roughness is apparently conserved under HF. Buffered HF solutions, however, attack the substrate more strongly with increasing pH. We have observed a significant increase in roughness. Moreover, the rod becomes broader (see Fig.) which is indicative of an increase of random step density. Further experiments will be aimed at determining the kinetics of the etching process.

X-RAY SCATTERING STUDY OF CHARGE DENSITY WAVE RELAXATION

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Contact: E. Isaac

We have studied the temperature dependence of the relaxation of the charge density wave (CDW) lattice upon application of a dc electric field by x-ray scattering. Fig. 1 shows the time dependence of the scattering amplitude of the CDW peak (13,0.7482,-6.5). It is similar to the behavior of the scattering intensity in a previous experiment [J. Zhang, et al., PRL **70**, 3095]. Fig 2 shows the temperature dependence of the relaxation rate. It is very sensitive to temperature. A similar behavior is observed for the electric field dependence of the relaxation rate.

Fig. 1 Time evolution of the scattering amplitude after application of an electric field.

Fig. 2 Temperature dependence of the relaxation rate of the CDW lattice after an electric field of 25 V/cm.

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Study of Sol-Gel PZT Precursor Structures by EXAFS

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The sol-gel processing route for the fabrication of ceramic materials offers numerous advantages over traditional powder forming methods, including significantly reduced temperatures for densification and better control of homogeneity by virtue of molecular level mixing. Materials corresponding to the $\text{Pb}(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ (PZT) compositions are of interest for the development of non-volatile computer memories and electrooptic modulators.¹ With much emphasis being placed on these materials for integrated device applications, a clearer picture of the structure of the material would serve as essential feedback in order to improve the quality and performance of the ceramic structures.

We take a molecular building block approach to ceramic synthesis. Our interest is in how short-range structure evolves into long-range structure through drying, thermolysis, densification and crystallization. We synthesized several PZT compositions by a method similar to that detailed by Budd.² After gelation and subsequent thermolysis, the "amorphous structure" of the sol-gel was examined by EXAFS spectroscopy. Absorption spectra were obtained from the Pb L₃, Ti K and Zr K edges from several sol-gels. Reference spectra of "model" compounds were obtained from absorption measurements on crystalline compounds as well as from FEFF5 calculations.³ Preliminary analysis of this data shows that the sol-gels can exhibit strong local order, including polymerization.

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Acid Corrosion of Cu(111) Surface

X16C

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We are interested in the corrosion process of copper on an atomic level. X-ray reflectivity is a suitable technique for the study of corrosion because it is sensitive on the atomic level, yet the sensitive length scales can be tuned over a wide range, from atomic level to relatively coarse (~ 1000 Å) scales.

A Cu(111) sample, spark cut from a common single crystal, was prepared by mechanical polishing followed by electropolishing. The sample was mounted in a specially designed cell with a thin ($6\mu\text{m}$) polypropylene window where an acid solution can flow over the sample and be drained, thus allowing the x-ray reflectivity measurements of the sample under a liquid *in situ*.

The reflectivity measurements were made by varying θ at constant values of 2θ . Before each set of measurement, a fresh solution of a new acid concentration was allowed to flow over the sample for several minutes and drained, leaving only a thin capillary film between the face of the crystal and the polypropylene window. Figure 1 and 2 below show the reflectivity at (0.1,0.1,0.1) of Cu(111) at the various concentrations of phosphoric acid (H_3PO_4). The wide shoulder is due to eclipsing of the incident and exit beams. The narrower peak riding on the shoulder is the reflectivity peak from a flat surface or interface. This surface peak increased with time in water and decreased as a weak phosphoric acid was introduced (Fig 1). However, the surface peak is restored by a more concentrated acid and destroyed by water (Fig 2).

Figure 1

Figure 2

This can be explained by the following scenario. In water, a relatively flat layer of copper oxide was growing into the copper crystal, so that the peak observed was due to the oxide/crystal interface. The weak acid started to dissolve the flat oxide layer, exposing once more a rough bare copper surface. However, as the concentration increased, the acid started to etch the copper surface. If the kinks and sharper regions tend to get etched first, this would lead to a flatter surface.

The treatments on the surface were not reversible; that is, the curve labeled '3' in Figure 1 was not reproduced upon treating with water after having treated with 0.2% phosphoric acid. The entire set of results was, however, reproducible after the electropolishing step was repeated. Since corrosion is an example of an electrochemical process, to do more accurate and reproducible experiment, the electrochemical potential of the sample must be controlled. This will be the next stage of this experiment.

X-17B1

Search for State Selected Photo-Fission of ^{235}U

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From experimental studies of proton and alpha induced fission of ^{235}U at deep sub barrier energies an argument has been made for the existence of a fission branch of about 1.5×10^{-4} in a low lying level around 100 keV in ^{235}U although from all known theoretical considerations the fission probability of this state is vanishingly small. To make a direct measurement of this branch it was decided to populate the level using photons of appropriate energy and then detect fission events resulting from its decay.

In a preliminary experiment at the NSLS X-17B1 hutch lasting from July 31 to Aug. 4 1993, a parallel plate avalanche counter (PPAC) was used to detect fissions when the white beam from the wiggler, attenuated by $0.5''$ Al + $0.5''$ Fe, was incident on a $200\mu\text{g}/\text{cm}^2$ thick metallic ^{235}U target. The target was contained within the PPAC for optimal geometric efficiency. The counter was made of aluminum and was operated with acetone at a pressure of 6 torr.. A potential of 100 V was applied across an inter-plate gap of 3 mm. The fission region of pulse heights was calibrated by using a paraffin moderated neutron source to induce fissions in the uranium.

With a starting electron ring current of 165 mA, 27 fission events were obtained in a counting time of 10000 seconds. Additional beam attenuations by $0.25''$ and $0.75''$ Fe gave 12 and 2 fission events respectively for the same counting time. A similar study with a tantalum target resulted in no fission detection. Although these results are qualitatively consistent with fission induced by a soft photon component, the observation of a significant inverse dependance of the efficiency of the counter for fission detection with incident photon flux made the interpretation somewhat ambiguous. The reduction in detection efficiency was probably due to space charge effects produced by excessive photo-electron production in the interaction of the beam with the high Z target. To be able to get quantitatively reliable results it is necessary to modify the PPAC so that the counter may be operated with full efficiency at all beam intensities. The detector has been suitably redesigned and is now ready for another run.

Atomic Structure of the AlPdMn Icosahedral Phase

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Two different data sets were collected on two different single grains of the quasicrystalline AlPdMn phase.

The superconducting wiggler beamline was equipped with a double Laue Si(220) monochromator and a Ge solid state detector. During the different runs, the energy stability of the instrument was very good, i.e., better than 2 eV at 24 keV. The intensity of standard reflections showed fluctuations of only 5% after normalization by the monitor.

In the first run, 150 reflections were measured at 20 and 1300 eV below the Pd edge. The sample was a fragment of a Bridgman ingot, presenting a narrow mosaic spread of about 0.01° (Fig. 1). A similar data set was previously carried out on a spherically ground single grain at beamline X3A2. However, the grinding process induced some damage to the sample, as evidenced by broad wings on the diffraction peaks. In that work, a phason Debye-Waller factor was seen in the Pd partial structure factor. It is therefore important to check that the effect is not due to the surface damage introduced by the grinding. As shown in Fig. 1, the sample used in this experiment is almost perfect, and in particular, does not show any tails in the peak profile. The agreement between the X3A2 and the X17B1 data sets is very good, with a reliability factor of 4%. In particular, the phason Debye-Waller factor is clearly seen in the X17B1 data set. This clearly demonstrates that the phason disorder, observed in these nearly perfect AlPdMn quasicrystals is intrinsic. It is further worth noting that the quality of the sample was high enough for extinction to be observable on the strongest reflections.

In a second run, a data set was collected at 80 keV on a spherically ground sample. The flux at this energy was comparable to that at 24 keV. About 100 reflections were collected at this energy. The agreement with the 24 keV data is satisfactory, with an R factor of 10%. (Note however that some of the difference could be due to the slight difference in f' values.) The same phason Debye-Waller factor is also seen in this data set. Further work is planned at high temperature, to study the phason dynamics.

IN SITU DETERMINATION OF THE OLIVINE, BETA AND SPINEL PHASE BOUNDARIES FOR Co_2SiO_4 AT HIGH PRESSURES AND TEMPERATURES

Laurence Galois (LMCP, U. Paris 6 and 7 and IPGP), Jianzhong Zhang and Robert C. Liebermann (CHiPR, ESS, SUNY at Stony Brook)

Phase transformations amongst the olivine, beta phase and spinel polymorphs of Co_2SiO_4 have been studied using *in situ* X-ray diffraction and a DIA-type, cubic-anvil high-pressure apparatus (SAM 85) at the superconducting wiggler beamline at the National Synchrotron Light Source (NSLS). Starting materials were powders of the olivine or spinel phases, previously synthesized in a 2000-ton uniaxial split-sphere apparatus (USSA-2000). Samples contained in BN capsules were compressed at room temperature to 7 to 9 GPa and then heated along P-T paths which crossed the spinel-olivine and spinel-beta phase boundaries at temperatures between 900 and 1200 C; conversion to the low-pressure, high-temperature phases occurred within 3-5 minutes. In the figures below, we illustrate the P-T paths along which reversal of the spinel-olivine phase boundary was obtained. These pilot *in situ* experiments demonstrate the feasibility of determining the phase boundaries and the olivine-beta-spinel triple point (near 6.5 GPa and 1000 C) more precisely than has been possible from quench-type studies (Akimoto and Sato, 1968; Rensberg and Liebermann, 1991), as well as studies of the kinetic rates of reactions amongst the polymorphs of Co_2SiO_4 .

Akimoto S. and Sato Y. (1968), *Phys Earth Planet Inter* **1**, 498.

Rensberg A.R. and Liebermann R.C. (1991), *Phys Chem Minerals*, **18**, 161.

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X17B1

COMPTON-ELECTRON SPECTROSCOPY USING HIGH-ENERGY
SYNCHROTRON RADIATION

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Compton-scattered electrons ejected from thin C and Al foils (10 and 20 $\mu\text{g}/\text{cm}^2$ thick, respectively) were detected at 0° with respect to the incident photon beam. Well-resolved Compton peaks were measured using monochromatic photons of 46 and 56 keV photons.

The left side of the figure below shows the experimentally measured electron spectrum generated by 56 keV photons scattered from the C foil with background subtracted. Also shown is a simulated spectrum obtained from the Monte-Carlo TIGER code. While there is reasonable agreement between these spectra on the low-energy side, the calculated spectrum does not include the broadening reflected by the Compton profile whose origin is in the momentum distribution of the bound electron. This is a potentially significant factor in the analysis of the performance of secondary electron transport in condensed matter for x-ray irradiation in the region of 10-100 keV. This is especially the case for the higher energy electrons because of the implied increase in electron range. The right side of the figure shows the same experimental spectrum in comparison with the Compton profile calculated within the impulse approximation. The centroid energy of the experimental peak is shifted down in energy because of the effect of electron transport.

Future experiments will involve investigation of resonant Compton behavior and coincidence measurements between the fluorescent x ray and ejected electron.

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X17B1

HIGH ENERGY X-RAY SCATTERING STUDY OF CRITICAL FLUCTUATIONS IN
 KMnF_3

J.P. Hill, J.-M. C. Gillet, S.M Shapiro and J.B. Hastings (BNL)

The cubic to tetragonal structural transition of the perovskites, exhibits unusual pretransitional effects; a sharp elastic component is observed in neutron inelastic spectra, appearing on top of the soft mode phonon peak. Additionally, x-ray scattering studies reveal the presence of two length scales in the critical fluctuations. Interest in this problem has recently been heightened by the discovery that the magnetic fluctuations of a number of antiferromagnets also occur on two length scales. Although it is believed that the second length scale is associated with defects, the phenomena remain poorly understood. In experiments performed with 8KeV x-rays, often only the sharp component is observed. This has led to speculation that it may be an intrinsic surface effect. It is possible, however that the number density of defects is simply higher in the near surface region.

The purpose of these experiments is to study the critical fluctuations of KMnF_3 utilizing high energy (60keV) x-rays to combine high x-ray resolution with neutron-like bulk penetration. In preliminary experiments, a sharp cubic-tetragonal transition was seen in a $10\text{mm} \times 10\text{mm} \times 3\text{mm}$ crystal at $T_C = 186.0 \pm 0.1\text{K}$. Operating in a transmission geometry the temperature dependence of the $1/2(331)$ R-point was studied. In contrast to the 8KeV data, the critical scattering immediately above T_C is comprised of two components, as shown below. The integrated intensity of the sharp component is smaller than the broad by two orders of magnitude. Further, the sharp component disappears within 1K of T_C ; it is observable in the 8KeV data up to $T_C + 4\text{K}$. The location in q-space of the sharp component allows one to determine if it is associated with cubic or tetragonal fluctuations. In future work, we hope to use the $\lambda/2$ harmonic to answer this question.

In conclusion, these first results demonstrate that high energy x-rays may contribute significantly to this long standing problem, in particular the large penetration depths allow bulk behavior to be probed directly at high resolution.

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Many rock salt type compounds, for example sodium chloride (NaCl), have been reported to transform to the cesium chloride structure under high pressure. Compressibilities of the rock salt type compounds are known to have a strong relationship to molar volumes at room pressure. However silver chloride (AgCl) has the rock salt structure at room pressure and its unit cell parameter ($a=5.5491\text{\AA}$) is very near to that of NaCl ($a=5.6402\text{\AA}$), the bulk modulus of silver chloride is larger than an expected value from the relationship and only a high pressure phase with a hexagonal cell has been reported, which was stable between 7.5 and 15 GPa. The aims of this work are to confirm the bulk modulus value of the AgCl with the rock salt structure and to search for a new high pressure phase using x-ray observations. The final goal is to discuss the different behavior between AgCl and NaCl based on crystal chemistry.

The high pressure behavior of AgCl was observed by an energy-dispersive x-ray diffraction method using a DIA type cubic anvil press (SAM85) combined with a 6 pole wiggler x-ray source (NSLS-X17B1). Pressure and temperature conditions were up to 13 GPa and 300 °C. The useful energy range for x-ray diffraction patterns was from 30 to 120 keV. In order to protect AgCl from a decomposition reaction to silver metal, AgCl was kept dry in a 6 mm cube, boron epoxy pressure medium. Pressure was calculated from volume of NaCl, which was separately encased in the pressure medium.

The rock salt structure was stable up to about 7.5 GPa and the bulk modulus was confirmed to be larger than that of NaCl. At around 8 GPa, x-ray pattern of AgCl became very complicated. However it was consistent with the reported hexagonal phase; its crystal system and unit cell parameters have not been determined yet. At about 12 GPa, the x-ray pattern became very simple. It may suggest a new high pressure phase transition. In a decompression process, the high pressure phase completely converted to the rock salt phase at lower than 7 GPa. The cesium chloride structure could not be found in this present pressure and temperature conditions. The different high pressure behavior between AgCl and NaCl may be explained by a square four coordination site preference of Ag^+ cation.

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In pelitic schists from southwestern Connecticut it's been observed that monazite (CePO_4) often appears to be pseudomorphed by fluorapatite. This texture is only observed when monazite is within biotite crystals which have been chloritized. In order to evaluate this reaction compositional line scans were conducted for both major elements (electron microprobe, SUNY Stony Brook) and rare earth elements (X17, NSLS). A single monazite crystal, 100 μm in diameter, was examined in thin section. Variations in major element composition can only be observed within the pseudomorphed outline of the crystal (Ca, F increase, Si, Mg, Fe, Al, K, and Cl decrease). Variations in REE can be observed in the surrounding chlorite for a 300 μm radius around the monazite crystal. Ce abundance in the chlorite matrix shows a significant and rapid increase from ~100ppm to 2000ppm at ~300 μm from the monazite edge. This may indicate REE diffusion during monazite breakdown. Figure below shows XRay spectra for chlorite ~300 μm from the monazite edge (~1000ppm Ce).

X17B1

PRESSURE-INDUCED PHASE TRANSITION IN PORTLANDITE, $\text{Ca}(\text{OH})_2$

Kurt Leinenweber, CHiPR, University at Stony Brook

Kruger et al. (1989) reported a crystalline to amorphous transition in the mineral portlandite, $\text{Ca}(\text{OH})_2$, at $11.7(\pm 1.1)$ GPa. The transition was reversible, with the amorphous phase reverting to the crystalline phase fully at $2.8(\pm 1.4)$ GPa. By comparison to other phases which show pressure-induced amorphizations, they inferred that the low-pressure $\text{Ca}(\text{OH})_2$ is metastable relative to a crystalline phase at high pressure. They did not observe the crystalline phase, however, because at room temperature it is kinetically inaccessible.

The present experiment was undertaken in order to find the new high-pressure form of $\text{Ca}(\text{OH})_2$. A sample of portlandite was raised to 8 GPa, and the temperature was increased. The powder x-ray pattern of the sample was observed with *in-situ* x-ray diffraction. At 200 °C a phase transformation began in the sample. The transformation went to completion by 300 °C. The temperature was raised to 400 °C to eliminate stresses which cause peak broadening, and a long x-ray exposure was taken at this temperature. The new phase has a more complex pattern than that of portlandite. We observed 25 x-ray lines between 1.5 and 3.4 Å (see Figure).

The new phase survived the quenching of temperature back to room temperature, and also persisted during partial decompression of the sample. However, at a low pressure prior to complete pressure release, the sample reverted to the portlandite form of $\text{Ca}(\text{OH})_2$. Therefore the new material must be observed *in-situ* at high pressure and temperature.

The new phase is similar to the amorphous form in that both revert to portlandite on pressure release. The amorphous phase may resemble the high-pressure phase in terms of local structure, and both phases have low activation barriers to portlandite formation.

Reference

Kruger M.B., Williams Q., Jeanloz R. (1989) Vibrational spectra of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ under pressure. J. Chem. Phys. 91, 5910-5915

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X-RAY STUDY AT HIGH PRESSURE AND TEMPERATURE OF A HOT-PRESSED POLYCRYSTALLINE SPECIMEN OF STISHOVITE: COMPARISON WITH POWDER SAMPLE

X17B1

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A polycrystalline specimen of stishovite (SiO_2 -rutile) was hot-pressed in a 2000-ton uniaxial split sphere apparatus (USSA-2000) at $P=10$ GPa and $T=1000^\circ\text{C}$ using amorphous silica powder as the starting material and recovered at ambient conditions. This polycrystalline specimen and a homogeneous powder of stishovite were simultaneously studied (in different parts of the same chamber) up to $P=12$ GPa and $T=1030^\circ\text{C}$ using *in-situ* X-ray diffraction and a DIA-type cubic anvil high pressure apparatus (SAM85) at the superconducting wiggler beamline of the National Synchrotron Light Source (NSLS). As the powder sample is compressed at room temperature, the individual diffraction peaks broaden, as a consequence of the elastic anisotropy of stishovite and the cold-pressing process. When the sample is heated under high pressure, the diffraction peaks sharpen and approach their initial shape above 400°C . In contrast, as the polycrystalline specimen is compressed to 12 GPa and subsequently heated to 1030°C , the diffraction peaks exhibit no broaden or sharpening. These data indicate that the deviatoric stress experienced by the individual grains in the polycrystalline aggregate is very low, which suggests that the deviatoric stress and strain within the polycrystal was minimized during the hot-pressing process. Consequently, we conclude that the single-crystal grains within this polycrystalline aggregate are well equilibrated (at least at 10 GPa and 1000°C) and the hot-pressed specimen is free of residual strain.

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MELTING TEMPERATURE OF COBALT IN THE PRESENCE OF DIAMOND

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Sintered diamond is a technologically important material and widely used in industry. Anvils made of sintered diamond have also been used in large-volume apparatus for high pressure experimental studies. A thorough knowledge of the physical properties of sintered diamond at high pressures and high temperatures is, hence, of significance for both science and technology.

In the present study, we observe the phase behavior of a mixture of diamond plus 10 wt. % of cobalt, that is, the composition of the sintered diamond, at simultaneously high pressures and high temperatures using x-ray diffraction. The experiments are conducted using a DIA-6 cubic-anvil high pressure apparatus (SAM85). The powdered diamond and cobalt mixture is loaded into the system and compressed by six WC anvils driven by a 250-ton press. NaCl powder is also loaded into the sample assembly as standard material for pressure measurements.

We measured the sample to a pressure of 8.5 GPa and a temperature of 1400°C. We found that the melting temperature of cobalt is lowered by the presence of diamond. The cobalt in the mixture melted at about 1200°C at 8 GPa. This temperature value is lower than the melting point of pure cobalt by over 300°C. Moreover, the value of 1200°C is exactly the temperature used in industry in sintering diamond. Thus, the melting of cobalt is likely playing an important role in the sintering process.

In addition to the melting, we have also observed the phase transition of cobalt from hcp to fcc. Such a phase transition happens at about 810°C at 8.5 GPa.

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P-V Equation of State of ZnV_2O_4 Spinel

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This study is to test the spinel ZnV_2O_4 for the possibility of an insulator-metal transition at high pressure. This transition is expected from trends occurring in transition-metal oxides which show metallic behavior for systems below a certain metal-metal distance, called the critical distance, and insulating for systems above. Goodenough predicted this distance in the early 60's to be 2.97 Å for vanadium $\text{V}^{3+}3d^2$ configuration. He has recently revised this distance to the range 2.89-2.91 Å. Such a transition, if it occurs, may be of first-order and detectable by x-ray diffraction studies.

The present study is conducted using a DIA-6 type cubic-anvil high pressure apparatus (SAM85). The ZnV_2O_4 sample is loaded into the system and compressed by six anvils. NaCl powder is also loaded into the sample assembly as standard material for pressure measurements. The x-ray diffraction pattern is collected using beamline X-17 at NSLS. We have measured the sample to 8.5 GPa and found the d spacings of the ZnV_2O_4 spinel decrease continuously with pressure. This means that no first-order phase transition happens in this material at the pressure range of this study. The P-V relation of this ZnV_2O_4 spinel has been derived from the present measurements.

In addition, we have found that the widths of the diffraction peaks increase with pressure. Such peak broadening can be partially kept to the ambient pressure after the sample is quenched from high pressure, as shown in the figure. This suggests that the peak broadening at high pressure is likely caused by both the deviatoric stress and crystal grain fining.

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IN SITU X RAY STUDY OF PHASE TRANSFORMATIONS IN THE SYSTEM $(\text{Mg, Fe})_2\text{SiO}_4$ X17B1

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Previous studies on the stability field of olivine, modified spinel and spinel in $(\text{Mg, Fe})_2\text{SiO}_4$ system were all based on quenched methods. Two major studies reported by Kawada (1979) and by Katsura and Ito (1988) resulted in conflicting conclusions concerning their geophysical meaning. *In situ* studies, therefore, become important.

We have studied phase transformations in the system $(\text{Mg}_{1-x}\text{Fe}_x)_2\text{SiO}_4$ with $x=0, 0.12, 0.20$, and 0.25 at pressures to 15.6 GPa and temperatures to 1260°C , using a cubic anvil apparatus (SAM85) that was interfaced with synchrotron x-ray radiation. In the *in situ* experiment, pressure was determined directly at every P-T condition with an uncertainty of ± 0.1 GPa, which is improved significantly over that of the quenched experiments (± 1 GPa). In addition, the phase assemblage can be determined during the experiment allowing run time reversals of univariant and invariant transformations. We reversed the α to β transformation at 13 ± 1.3 GPa and 1000°C for Mg_2SiO_4 . This pressure is about 1 GPa less than that reported by Katsura and Ito, but agrees well with that determined by Kawada. For compositions with $x=0.12, 0.20$ and 0.25 , both *in situ* observations and compositions determined on quenched samples basically agree with that of Kawada but not that of Katsura and Ito. The figure illustrates our preliminary constraint on the univariant boundary of $(\text{Mg, Fe})_2\text{SiO}_4$ system. We also plot the data of the two previous studies for comparison.

This work was supported by the National Science Foundation under a grant to the Center for High Pressure Research (CHiPR).

HIGH PRESSURE AND HIGH TEMPERATURE X-RAY DIFFRACTION STUDIES OF ZrO_2 USING DIA-6 APPARATUS AND SYNCHROTRON RADIATION X17B1

Li Chung Ming (University of Hawaii), Keiji Kusaba and Xiaoyuan Li (SUNY at Stony Brook)

Phase transformations and the isothermal compression of ZrO_2 have been studied at pressures up to 9 GPa and at temperatures up to 500°C using DIA-6 apparatus (SAM85) interfaced with synchrotron radiation at Beamline X17B1 at NSLS. High quality diffraction spectra were obtained in 300 seconds. The figure shows energy dispersive spectra at ambient and high pressure and temperature conditions. Sample pressure was determined using NaCl as an internal pressure standard and temperature was monitored using a Chromel/Alumel thermocouple placed near the center of the sample chamber. Some interesting observations are: (1) The monoclinic $\text{ZrO}_2(\text{I})$ phase transforms into the orthorhombic $\text{ZrO}_2(\text{IV})$ at ~ 3.1 GPa and at room temperature. (2) The transformation of $\text{ZrO}_2(\text{I})$ into $\text{ZrO}_2(\text{IV})$ at room temperature is reversible and very sluggish such that the $\text{ZrO}_2(\text{I})$ persists to 9.4 GPa, the highest pressure in this experiment; and the $\text{ZrO}_2(\text{IV})$ persists down to 1 bar during the unloading process. (3) When the sample was heated to 500°C at 9.4 GPa, all the $\text{ZrO}_2(\text{I})$ phase was converted into $\text{ZrO}_2(\text{IV})$ phase. A single phase of $\text{ZrO}_2(\text{IV})$ can thus be obtained and persists when quenched from 500°C at 9.4 GPa. (4) During the unloading process, the $\text{ZrO}_2(\text{IV})$ phase partially converts back into $\text{ZrO}_2(\text{I})$ at pressures below 2.4 GPa. Therefore, a single phase of $\text{ZrO}_2(\text{IV})$ can not be retained at the ambient conditions.

On the basis of the high quality spectra obtained for both the $\text{ZrO}_2(\text{I})$ and the $\text{ZrO}_2(\text{IV})$ phases, it is anticipated that reliable isothermal compression data will be derived. Such a data analysis is under way.

This work was supported by the National Science Foundation under a grant to the Center for High Pressure Research (CHiPR).

DEHYDROXYLATION OF Mg-RICH CHLORITE AT 2.5 AND 4.1 GPa

X17B1

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The interlayer dehydroxylation reaction of a natural 11b clinochlore was studied at pressures of 2.5 and 4.1 GPa using the SAM 85 multiple anvil device. Heating chlorite at ambient pressures will cause interlayer dehydroxylation where half or more of the OH groups are lost, resulting in the "modified chlorite structure" (Brindley and Ali, 1950).

Previous studies (Bai et al., in press) of the same material using a high pressure differential thermal analysis device found that in open capsule experiments the clinochlore undergoes interlayer dehydroxylation to form a modified chlorite structure and water vapor, with the reaction being nearly isothermal (690 °C) above 100 bars. These experiments were conducted up to 770 bars. The behavior of chlorite at Earth mantle conditions may be quite significant in understanding dewatering processes of subducting lithospheric plates.

In this study the behavior of the X-ray diffraction patterns upon dehydroxylation were different than that seen by Bai et al. However, they were collecting diffraction data on quench products rather than making in situ measurements. Initiation of dehydroxylation is suggested by time-variant diffraction patterns at a given temperature and eventual failure of the thermocouple due to water vapor in the system. At 2.5 GPa dehydroxylation occurs at approximately 680 °C whereas at 4.1 GPa it occurs at 675 °C. These results do not vary, within experimental error, from the results at 100 bars, suggesting zero or slightly negative slope to the P-T curve at these pressures.

Brindley, G.W. and Ali, S.Z. (1950) X-ray study of thermal transformations in some Magnesium chlorite minerals. *Acta Cryst.*, 3, 25-30.

Bai, T. B., Guggenheim, S., Wang, S.J., Koster van Groos, A.F., and Rancourt, D.G. (in press) Metastable phase relations in the chlorite-H₂O system.

BEHAVIOR OF ANKERITE, Ca(Fe,Mg)(CO₃)₂, AT HIGH PRESSURE

X17B1

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In situ energy-dispersive X-ray diffraction experiments were conducted on ankerite in a large-volume multi-anvil apparatus (SAM85) over the pressure range from 0 to 8.5 GPa. White-beam synchrotron radiation was used from the superconducting wiggler port at beamline X17 of the National Synchrotron Light Source, Brookhaven National Laboratory. Three samples were layered in a hole in the boron plus epoxy pressure medium. The ankerite powder specimen was placed at one end, a specimen of ZnV₂O₄ (reported on in Li, *et al* earlier in this volume) was placed at the other end, and NaCl powder, used for an internal pressure standard, was placed between the two specimens. All experiments were conducted at room temperature.

The ankerite sample, having composition Ca_{1.0}Fe_{0.73}Mg_{0.27}(CO₃)₂, shows strongly anisotropic compression, with *c* undergoing greater compression than *a*, as expected. No evidence is found for a structural phase transition that had been considered likely on the basis of ankerite's structural similarity to calcite, which undergoes two displacive phase transitions at high pressure. Previous X-ray diffraction experiments up to 4 GPa in a diamond-anvil cell also failed to show evidence of a phase transition in both ankerite and isostructural dolomite. It was expected that within the higher pressure range of the present experiments, a phase transition may occur. Although it is possible that the failure to observe a phase transition could be attributed to a kinetic hindrance associated with the ambient temperature of the experiment, no such effect has been observed for the displacive phase transitions in calcite.

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P-V-T EQUATION OF STATE FOR IRON AND MAGNESITE

X17B1

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The P-V-T data for iron is essential in modeling the iron phase transitions as noted in recent laser-heating experiments (Saxena et al., 1993). The relative low-pressure/high-temperature P-V-T data constrain the temperature and pressure dependences of the bulk modulus and thermal expansion. The P-V-T data on magnesite are important in understanding the stability of magnesite in the mantle and its role as a store-house of CO₂.

We have measured the cell dimensions for bcc-iron, fcc-iron, and magnesite over a temperature range of 25 to 900 °C and pressures between 1 bar and 8.5 GPa. The experiments were performed using a DIA-type cubic anvil apparatus (SAM-85) at X-17B1 beam line of the National Synchrotron Light Source (NSLS). Iron powder was used as the starting material and compressed by tungsten carbide anvils. Synthetic magnesite was included in the same container separated from iron by a salt layer which was used as an internal pressure standard. In situ P-V-T measurements of cell dimensions for magnesite were carried out successfully without any noticeable break-down of magnesite up to 900 °C and 7.0 GPa.

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X17B1

MICROPLANAR BEAM RADIOTHERAPY [MRT] OF MALIGNANT BRAIN TUMORS IN RATS

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Microplanar beam (microbeam) radiation therapy [MRT] of brain tumors uses multiple microscopically thin, macroscopically wide beams of x rays to reduce concomitant damage to normal brain structures¹. Right frontal 9L gliosarcomas of the Brookhaven National Laboratory [BNL] strain² were initiated by 1 μ l injections of 10⁴ cells suspended in culture medium 4 mm beneath the skull in 57 ~200 g rats. MRT was done 14 d later on 44 of these rats using a fixed 4 mm-high, 25 μ m-thick, 0.25 mm Gd-filtered microbeam (critical energy = 48.5 keV) in the X17B1 hut when tumor diameters were ~4 mm and the median residual lifespan [MRL] of the untreated 13 rats was 7 d. Skin-entrance absorbed dose [SED] rates were ~400 Gy·s⁻¹. Each unidirectional 10 mm-wide x 12 mm-high rectangular irradiation array (100 3-tiered 12 mm-high x 25 μ m-thick quasiparallel microplanar fields separated at 100 μ m intervals, field center-to-field center) required 300 exposures, 100 successive exposures in each of 3 tiers. An anesthetized rat was aligned with and exposed to the microbeam then moved either 100 μ m laterally in a tier or 4 mm vertically to the next tier before each of the following 299 equal exposures. Using this array to straddle tumors anteroposteriorly with SED = 625 Gy/exposure, 4/14 rats were alive 75 d after irradiation (MRL = 28 d) whereas 11/15 or 8/15 rats were alive 75 d after the tumors were crossfired first anteroposteriorly and then transversely from right to left using the same array and either 625 Gy or 312 Gy per exposure, respectively.

MRT for pediatric brain tumors³ at the Medical and National Synchrotron Light Source [NSLS] Departments of BNL will be approached initially through follow-up of these rats to 100±1 d after MRT, then through analogous experiments on other rats and on immature baboons. Choices of SED will be guided by Monte Carlo microdosimetric computations. Particular attention will be given to the cardiosynchronous pulsation of primate brains⁴.

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Biological Effects of Auger Electrons from Indium, Induced by Monochromatic Synchrotron X-rays

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The specific aim of the project is to investigate biophysical effects and determine the relative biological effectiveness (RBE) from Auger electrons emitted from Indium, incorporated into the nucleus of cells. In this experiment Auger cascades are induced by monochromatic x-rays with energies just above the K-shell absorption edge for indium at 27.94 keV.

Auger electron emission is an atomic shell effect important for basic biophysical research, radiobiology, radiation protection, and treatment of cancer. Several radiobiological experiments, *in vitro* and *in vivo*, have repeatedly emphasized that when a decay (electron capture or internal transition) occurs inside or very near the DNA double helix, the dense shower of Auger electrons damages molecules near the decaying atom severely. This is due to the highly localized energy deposition around the decay site. So far most experiments to determine the RBE of Auger electron emission have been performed using radionuclides which apart from Auger electrons also emit γ -radiation, characteristic x-rays or conversion electrons during the decay. This makes the interpretation of previous experiments difficult and the RBE determination for the Auger electrons less accurate. Irradiation with monoenergetic photons with energies straddling the K-shell absorption peak should make it possible to separate the effects caused by primary radiation and Auger electrons.

A pilot study on cultured V79-CH cells was performed at the X17B1 beam line to optimize cell irradiation parameters and measurements of the absorbed dose. Calibrated termoluminescent dosimeters (TLD:s) was used for dosimetry and the stability of the beam was checked continuously by two argon-filled ionization chambers. Two photon energies just above and below the K-edge of indium were used. During this first experiment we obtained preliminary survival curves for the cells under normal conditions. These results are now analyzed for optimizing the next experiment to study the Auger effect. The absorbed dose measurements must be improved by direct simultaneous measurements at the cell pellet irradiation point in order to avoid misinterpretation of the cell results. It can be concluded, that our results show that this technique provides a good opportunity to investigate the biological effects of Auger emission and determine related RBE factors.

This investigation is supported by the Swedish Cancer Foundation (Grant # 2353-B93-07XAB), the Swedish Radiation Protection Institute (SSI P 738.93) and the U.S. Dept. of Energy under contract # DE-AC02-76CH00016.

EQUATION OF STATE OF MgO AT HIGH PRESSURES AND HIGH TEMPERATURES

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The NaCl scale has been generally used to measure the pressure values generated with multianvil type high pressure apparatus combined with x-ray sources. Recently, because of the development of the high pressure technology, the pressure and temperature region attainable with the multi-anvil system has been largely extended. This situation created various problems in NaCl pressure markers especially at high temperatures. The melting temperature of NaCl is low and above the melting temperature, it does not work as a pressure marker at all. Even below the melting temperature, it has become difficult to use the NaCl scale because of the crystal grain growth which causes inaccuracy in the x-ray diffraction. As the next candidate for a pressure standard, MgO has been proposed. This has a high melting temperature at high pressure. In order to use MgO as a pressure standard, we must know the accurate equation of state of MgO in a wide range of pressures and temperatures. Several equations of state have been proposed based on theoretical study, diamond anvil experiments, or the shock experiments. However, there are considerable discrepancies among them, and very precise measurement is required.

Using the DIA type cubic anvil apparatus (SAM85) at the X17B1 beam line, we have observed the powder x-ray diffraction profiles of MgO and measured its volume under various pressure and temperature conditions (up to 10 GPa and 1200°C). The data so far obtained is now in analysis, and the basic pressure and temperature capability of the SAM system will make it possible to obtain a precise equation of state of MgO in a wider P-T conditions.

This work was supported by the National Science Foundation under a grant to the Center for High Pressure Research (CHiPR).

ANGLE DISPERSIVE X-RAY DIFFRACTION OF MOLYBDENUM IN A LARGE VOLUME HIGH PRESSURE APPARATUS: FIRST RESULTS USING MONOCHROMATIC RADIATION

X17B1

Michael T. Vaughan and Keiji Kusaba, CHiPR, SUNY at Stony Brook

Preliminary diffraction measurements have been made on a foil of molybdenum using ~45 keV monochromatic radiation from the X17 superconducting wiggler. This monochromator can be tuned from ~20 TO ~90 keV. The uniform absorption of the sample to a monochromatic beam makes such data much more tractable for the intensity measurements required for structure refinements.

Although this experiment was conducted at ambient conditions, it was performed using a DIA-type cube anvil press (SAM85) and serves as a preliminary study for making such measurements at high temperatures and pressures.

After initial alignment runs, a spectrum was obtained by scanning 2θ from 7° to 20° with intervals of 0.025° . Counting time of 8 seconds per step was used. Afterwards, four peaks were scanned with a smaller step ($.01^\circ$) and a longer counting time (20 seconds). Beam time constraints precluded spending more time. This data is presented below in Figure 1. Figure 2 shows an energy dispersive spectrum from the same sample.

MORE ON PHASE RELATIONS OF CaSiO_3

Yanbin Wang and Donald J. Weidner (SUNY at Stony Brook)

At pressures between 8 and 10 GPa, CaSiO_3 is known to break down into two phases, with compositions Ca_2SiO_4 and CaSi_2O_5 , respectively. X-ray data on the quenched samples suggested that they were both monoclinic, with larnite (β) and a titanite-like structure, respectively (1). In our *in situ* study on the phase relations for CaSiO_3 , several samples were back transformed from perovskite to the two-phase mixture (2). Transmission electron microscopy on the recovered specimens revealed pervasive twinning in both Ca_2SiO_4 and CaSi_2O_5 , suggesting possibility of structural phase transitions. Thus, Ca_2SiO_4 (olivine) was prepared and studied further using the DIA-apparatus at a pressure of 9 GPa and temperatures up to 1300°C . X-ray diffraction spectra indicate that larnite appears during heating at temperatures as low as 300°C and remains stable until about 1050°C , at which temperature an abrupt change in the diffraction patterns is observed. These patterns can be tentatively indexed as orthorhombic, whose c-axis is roughly 3 times the larnite b-axis. All 20 major diffraction lines observed at 1100°C can be fitted to yield $a = 5.541(7) \text{ \AA}$, $b = 9.385(11) \text{ \AA}$, and $c = 20.529(27) \text{ \AA}$. Such an orthorhombic phase (the so-called α'_L phase) has been known to occur in Ca_2SiO_4 at 1 bar (3, 4). Previous study on Ca_2SiO_4 was based on DTA analysis and only to 0.7 GPa (4). Thus, our data have extended the α'_L - β boundary to 9 GPa. Since the α'_L - β transition is non-quenchable, previous quench studies on CaSiO_3 were not able to detect the α'_L field. Figure shows portion of the CaSiO_3 phase diagram based on our new data and that of (2) and (5).

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YIELD STRENGTH OF MgSiO_3 PEROVSKITE AT HIGH PRESSURE AND TEMPERATURE

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The yield strength of MgSiO_3 perovskite was measured up to 9 GPa and 800 °C using the DIA-apparatus. The technique of using peak shape analysis to obtain information on microscopic strain was described by (1) and (2). A sintered polycrystalline perovskite specimen was crushed under liquid N_2 to $\sim 30 \mu\text{m}$ particles (individual grain size about $10 \mu\text{m}$), compressed at room temperature to 9 GPa, and then heated under constant load. NaCl was used as pressure marker. The microscopic strain from peak broadening for the 111 and the triplet (020, 112, and 200) diffractions is analyzed. As pressure is increased, the strain for the (112) diffraction increases rapidly then remains roughly constant above 6 GPa, suggesting that the sample has reached its yield point. The strain for the (111) diffraction shows little indication of yielding and increases nearly linearly with pressure. Upon heating, the strains decrease monotonically with temperature to 800 °C, where the sample began to transform to the low pressure phase enstatite. By using the isotropic aggregate Young's modulus of the perovskite, the strains are converted to deviatoric stress (Figure), which represents a statistically averaged differential stress acting normally on the diffraction planes in a direction sub-parallel to the diffraction vector. The deviatoric stress for the (111) diffraction may not represent yield strength below about 200 °C. The large difference in yield strengths in the directions normal to the (111) and (112) planes at low T may be attributable to twinning on the {112} planes; the (1-12) and (11-2) twin planes are about 11° and 37° from the (112). It is interesting to note that the microscopic strain (0.83%) for 112 is about twice that of the "spontaneous strain" $(a^2+b^2)^{1/2}/c-1 = 0.49\%$.

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Reversal and Kinetics of the Coesite-Stishovite Phase Transformation

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Phase transformation between coesite and stishovite has been extensively used for pressure calibration at high temperature in multianvil apparatus. However, no true reversal of the phase transformation boundary has been obtained. Using a DIA-type cubic anvil apparatus (SAM-85) at the X-17B1 beam line of the National Synchrotron Light Source, we have investigated phase relation of SiO_2 up to 120 Kb and 1430 °C using synthetic coesite and stishovite powders as the starting materials. The phase transformation between coesite and stishovite was identified by a change in the relative intensity or by observing the first appearance of a phase that did not already exist. Experimental results are shown in Fig. 1 and compared with those of Yagi and Akimoto (1976) and Zhang et al. (1993) in Fig. 2. In most experiments the diffraction patterns on samples were collected every 10 to 15 minutes. On this time scale, the phase transformation between coesite and stishovite was able to be reversed within a pressure range that is less than 4.0 Kb at temperatures above 1100 °C, resulting in an equilibrium phase boundary for the coesite-stishovite transition that can be described by an equation $P(\text{Kb}) = 65 + 0.022T(^{\circ}\text{C})$. At temperatures below 1100 °C, however, the phase transformation is strongly kinetically controlled, in the sense that the pressure interval between the observed and extrapolated equilibrium phase boundaries was observed to increase significantly with decreasing temperature. This result is most probably due to the large energy barrier associated with the change on Si^{4+} coordination between 4-fold and 6-fold. It is also likely that this pressure interval will be a function of time scale, making it very difficult to unambiguously determine the equilibrium phase boundary below 1100 °C; note that all of the Yagi and Akimoto (1976) data are for temperatures less than 1100 °C.

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In-Situ X-ray diffraction study of the Fe(bcc)-Fe(fcc) Phase Transition

X17B1

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The Fe(bcc)-Fe(fcc) transition is an important part of the phase relations of iron that are critical for the understanding of the Earth's core. As many of the results for this transition were obtained by electrical resistivity measurements (e.g., Bundy, 1965), limited data are available from in-situ X-ray diffraction observations (Akimoto et al., 1987). In this work, we performed high pressure and temperature experiments using the DIA-type cubic anvil apparatus (SAM-85) at X-17B1 beam line of the National Synchrotron Light Source. Iron powder was used as the starting material and compressed by tungsten carbide anvils with NaCl as an internal pressure standard.

Our experimental results for the Fe(bcc)-to-Fe(fcc) transition are in good agreement with those of Akimoto et al. (1987) (see Fig. 1). However, the Fe(fcc)-to-Fe(bcc) transition was observed to be kinetically controlled in the sense that the transition becomes increasingly sluggish with increasing pressure. At pressures below 4 GPa, the Fe(bcc)-Fe(fcc) transition was reversed when temperature was changed by 25-30 °C; at 6, 7 and 8 GPa, the Fe(fcc)-to-Fe(bcc) transition was observed, respectively, around 400, 200, and 100 °C on a time scale of 10 to 15 minutes. At room temperature the rate for the Fe(fcc)-to-Fe(bcc) transition increased when pressure decreased from 8 to 5 GPa, but this transition was not complete in a period up to four hours. As a result, Fe(fcc) could be recovered in this pressure range at room temperature. We note that all these observations were not reported by Akimoto et al. (1987).

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X17B2
ARTERIAL CROSS-SECTION MEASUREMENTS FROM DUAL ENERGY TRANSVENOUS CORONARY ANGIOGRAPHY IMAGES

Dean Chapman (NSLS)

The synchrotron based coronary angiography project at the National Synchrotron Light Source obtains images of the coronary arteries with a venous injection of an iodine contrast agent. Two monochromatic x-ray beams whose energies are just above and below the iodine K-absorption edge are used to image the coronary artery system resulting in two simultaneous images with overlapping pixels. This allows two areal mass densities to be calculated from these images; one of iodine and one of water. Analysis procedures have been developed to arrive at these areal mass densities with corrections to the values being made for detector cross-talk and beam harmonics. The resulting absolute iodine areal mass density image or "iodine map" can be used 1) to give a "third" dimension or thickness information to the image and 2) to give a relative arterial cross-sectional area by a line integration across an arterial feature. If an absolute arterial dimension is known from another projection or previous arteriogram then the absolute area can be calculated, otherwise the relative areas are determined.

Results are shown for an image taken of a 66 year old female whose previously blocked right coronary artery was opened by balloon angioplasty 2.5 years prior to this image. The image is shown below on the left. The right coronary artery is clearly seen extending to the left from the aorta. The boxed region shows where the blockage occurred and a narrowing still exists. This region is processed into a rectangular image which is shown at the lower right. The plot (upper right) shows transverse line integrals across the image to indicate the relative cross-sectional area of the artery where the blockage occurred and shows a greater than 50% areal reduction in that region.

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Modulation Transfer Function measurements of the new Si(Li) angiography detector X17B2

C. Schulze (ESRF) and D. Chapman (NSLS)

The modulation transfer function (MTF) of the new 250 μ m angiography detector system was determined by means of the edge spread function method and directly using a square-wave chart. Making the edge out of iodine and giving it a wedge shape allowed the measurements of the MTF of the subtraction signal as well as a possible contrast dependence of the MTF of the high energy, low energy and difference signals.

The cavity in the Lucite wedge was filled with a 185 mg/ml iodine solution. The right-angled wedge was mounted on the patient chair with its apex horizontal, the flat side normal to the x-ray beam. The I-filled cavity thus provided two edge signals in the horizontal plane of the beam, of which the contrast changed when the wedge was scanned vertically using the chair. Edge spread functions (ESF) were also measured diagonally, by tilting the wedge by 45° around the axis of the beam. The square-wave chart was a standard Pb chart of 0.1 mm thickness mounted normal to the beam at the patient position.

To obtain the MTF, the derivative of the measured ESF is taken yielding the line spread function (LSF). The modulus of its Fourier transform then gives the MTF. A prior normalization of the LSF provides unity of the MTF at zero frequency. The operations are carried out on a gaussian fit of the data. This eliminates high frequency noise as well as a positive bias due to aliasing because of the finite sampling interval of 250 μ m. The measured square wave transfer functions $M_1(\omega)$ have to be corrected by a series of square waves yielding an approximation of the true MTF: $MTF(\omega) = \pi/4 (M_1(\omega) + 1/3 M_1(3\omega) - 1/5 M_1(5\omega) \dots)$, where ω represents the fundamental frequency. Owing to the low Nyquist frequency of the system a full correction is not possible.

Figure 1 shows the horizontal MTF of the imaging system, derived from the edge spread function of the vertically oriented wedge, measured at detector gain 6. Since no significant contrast dependency is found the data is averaged over several rows. Furthermore, the harmonic contamination of the beams, varied by means of different absorbers and different detector gains, does not influence the resolution of the detector system within the limits of the accuracy of the measurements. The MTF of the subtraction signal still amounts to 25 % at the Nyquist frequency. It was found to be slightly smaller than those of the energy signals.

The results from both methods agree well for high and low energy signals. The vertical SWC and the diagonal wedge measurements reveal an inferior resolution of the high energy beam, which can be explained by its bigger vertical cross-section at the patient position. This is represented in fig. 2.

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IMAGING OF A MAMMOGRAPHIC PHANTOM WITH 33 KEV SYNCHROTRON RADIATION X-RAYS

H.D. Zeman, F.A. DiBianca, and G. Lovhoiden (University of Tennessee, Memphis)

On November 13-14, 1992, the first running time was available on X17 to test the UT CCD X-ray imaging system with a mammographic phantom and monochromatic X-rays. The X-ray energy on X17B2 is 33 keV, which is really too high for mammographic imaging. However, much progress was made during this run in developing an imaging procedure and improving the performance of the imaging system. The UT CCD X-ray imaging system uses an Astromed liquid nitrogen cooled slow scan CCD with 384 x 578 pixels each 0.022 x 0.022 mm in size. The CCD is coupled to a Lanex Regular X-ray intensifying screen with a 45° mirror and a Ilex Oscillo-Paragon 80 mm f 1.3 macro lens optimized for 2:1 demagnification. The CCD and mirror are mounted on a three axis stepper motor driven translator, which allows computer controlled adjustment of camera field and focus. For the November studies, the CCD camera system, and the mammographic phantom to be imaged were mounted on the Patient Chair in the X17B2 Radiography Room. The distance between the intensifying screen and the phantom could be adjusted from 10 - 100 cm, and a scatter reducing slot aperture could be placed between the phantom and the screen. The scan rate was set at 3 cm/sec, and 9 frames were used to expose the CCD system. The monochromator was unbent to produce a 2 mm high X-ray beam, and absorbers were placed in the beam to reduce the total skin dose to about 3 Rads for the phantom. In spite of the slow scan rate and multiple frames some residual horizontal banding was visible due to variations in X-ray flux. This banding was removed using calibrating data on the image frame. A beam monitor will be added to the system for the next run. Because of the high X-ray energy, the resulting images were very low in contrast, and significant noise was present. A comparison was made between the CCD imager, which has a pixel size of 0.044 x 0.044 mm, and the LBL Si(Li) detector, which has a pixel size of 0.500 x 0.450 mm. The same phantom was imaged at roughly the same X-ray dose. The CCD image was binned so that 11 x 11 pixel regions were averaged together, giving a pixel size of 0.484 x 0.484 mm, closely matching the LBL Si(Li) detector. A small piece of the image taken with the Si(Li) detector was chosen that closely matched the section covered in the CCD image. This comparison is shown below.

The CCD image is on the left and the Si(Li) image is on the right. The CCD image appears to be somewhat noisier than the Si(Li) image which is not unexpected for such a low contrast object, since the CCD has the additional noise contributions of readout noise, and light quantum noise. Also, the calibration data for the CCD image was taken from a single CCD image of a 6 cm thick Lucite and water absorber, while the calibration data for the Si(Li) image was the average of many single line scans. In future experiments, multiple calibrations images will be used with the CCD imager as well. An optical design effort is underway at present at UT, with the goal of increasing the optical efficiency of the CCD imager by about a factor of five, which should yield X-ray quantum limited images comparable to those produced with the Si(Li) detector.

General User Beam Time has been allocated to this experiment for the summer of 1993. During this run image quality will be measured vs. X-ray energy. The dose rate will be measured using ionization chambers and TLD's. The quantum efficiency of the CCD imager will be measured with three different intensifying screens, namely: the Kodak Lanex Regular screen, a Kodak Min-R Medium mammographic screen, and a CsI(Tl) crystal 3 mm thick and 100 mm in diameter. The effect of light quantum noise will be observed by measuring the noise level vs. the lens opening. The different screens will be compared at different X-ray energies for image quality.

EQUATION OF STATE OF MAGNESIUM OXIDE TO 227 GPa

T. S. Duffy, R. J. Hemley, and H. K. Mao (Geophysical Laboratory, CIW)

Magnesium oxide (MgO) is significant because of its wide use as an internal standard in high-pressure experiments as well as potentially being a major constituent of the earth's lower mantle. The equation of state of MgO was studied by x-ray diffraction to 227 GPa at room temperature. Compression of a mixture of MgO and molybdenum powder was carried out in a Mao-Bell diamond anvil cell using beveled diamonds with a central flat of 20 μm . Pressures were determined using the measured volumes and shock wave isotherm of Mo. Volumes of MgO were calculated from the (200) and (220) diffraction lines.

It was found that MgO remains in the sodium chloride (B1) structure up to the highest pressure studied, in agreement with *ab initio* calculations. Fitting the data to a third-order Birch-Murnaghan equation yields a bulk modulus of 176(4) GPa and a pressure derivative of 3.8(1) (Fig. 1). MgO is slightly more compressible than predicted from extrapolation of low-pressure ultrasonic data. The compression curve for MgO agrees with an isotherm derived from shock data to better than 1.5% over the range studied. Comparison of the present isotherm with density and temperature measurements under shock compression allows the thermal expansivity, α , to be constrained at high P and T. At 169-196 GPa, $\alpha = 8-9 \times 10^{-6} \text{ K}^{-1}$, which is 20-30% lower than previous results based on extrapolated ultrasonic data. Above 100 GPa, the lattice parameters for the (200) and (220) lines of MgO diverge by up to 0.3%. This is likely to be a consequence of material strength or possibly structural distortion.

This work was supported by NSF and DOE.

EQUATIONS OF STATE FOR Au, NaCl, Fe_xO, AND MgO AT HIGH TEMPERATURES

Y. Fei, H. K. Mao, J. F. Shu, and J. Z. Hu (Carnegie Institution of Washington/Geophysical Laboratory)

A double-heater high-temperature diamond anvil cell (Figure 1a) has been developed to observe phase transitions and to obtain volumetric data under simultaneous high *P-T* conditions. The high-temperature diamond cell is capable of reaching simultaneous temperature and pressure of 1100 K and 50 GPa. By using the high-temperature diamond cell and synchrotron X-ray diffraction techniques, isothermal compression curves of a number of materials such as Au, NaCl, MgO, and Fe_xO have been determined at high temperatures. Figure 1b shows representative energy-dispersive X-ray diffraction patterns of a mixture of Au, NaCl, and MgO as a function of pressure at temperature of 700 K. The *P-V-T* data of Au and NaCl indicate that pressures calculated from the existing equation of state of Au are higher than those calculated by using equation of state of NaCl by about 0.5 GPa at high temperatures. The high-temperature diamond cell was also used for in situ determination of high *P-T* phase transition boundary. Figure 1c shows the phase diagram of wüstite Fe_{0.92}O determined by in situ X-ray diffraction at high *P-T*. The transition in wüstite was also investigated by using single-crystal X-ray diffraction technique. The high-pressure phase of wüstite is rhombohedral. A reversible phase transition from cubic to rhombohedral structure was observed at 17 GPa at room temperature under hydrostatic condition. The volume-pressure relations of wüstite at room temperature are shown in Figure 1d.

Fig. 1. a. Configuration of a double-heater high-temperature diamond anvil cell. b. Representative energy-dispersive X-ray diffraction patterns of a mixture of Au, NaCl, and MgO as a function of pressure at temperature of 700 K. c. The phase diagram of wüstite Fe_{0.92}O determined by in situ X-ray diffraction at high *P-T*. The arrows indicate the experimental *P-T* path. d. The volume-pressure relations of Fe_xO at 300 K.

Volume as a function of pressure, $V(P)$, for $\text{HgBa}_2\text{CuO}_{4+\delta}$ to 10 GPa

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Recently, $\text{HgBa}_2\text{CuO}_{4+\delta}$ ¹ has been found to be superconducting with transition temperature, T_c , around 90 K. Knowing the transition temperature as a function of volume, $T_c(V)$, helps us to understand the superconducting mechanism in light of several theoretical models.² We have measured $T_c(P)$ for $\text{HgBa}_2\text{CuO}_{4+\delta}$ to 4 GPa.³ The observed values of $T_c(P)$ can be transformed into $T_c(V)$ if $V(P)$ is known. We have carried out the energy dispersive diffraction for $\text{HgBa}_2\text{CuO}_{4+\delta}$ at various pressures to 10 GPa using the Mao-Bell type diamond anvil cell. We used silicone oil as a pressure medium for this study, because the polycrystalline $\text{HgBa}_2\text{CuO}_{4+\delta}$ undergoes decomposition in methanol:ethanol::4:1. Pressure is determined from the shift in ruby fluorescence peaks. Figure 1 shows the diffraction pattern for $\text{HgBa}_2\text{CuO}_{4+\delta}$ at 1.1 GPa. We have obtained $a(P)$ and $c(P)$ where a and c are the lattice parameters. In summary, Fig. 2 shows $V(P)$ for $\text{HgBa}_2\text{CuO}_{4+\delta}$ to 10 GPa.

Fig. 1

Fig. 2

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New High-Pressure Transformation in α -Quartz*

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Upon room-temperature static compression in a Mao-Bell megabar-type diamond-anvil cell (neon medium), energy-dispersive synchrotron x-ray diffraction of polycrystalline α -quartz is found to give the quartz structure to about 20 GPa (Fig. 1). With continued compression, there is a sudden loss of some quartz peaks, a shift of other quartz peaks, and the appearance of new features in the diffraction pattern. A sharp change in the character of the Raman spectrum also occurs at 21 GPa, marked by weakening and broadening of the α -quartz A_1 and E modes (Fig. 2), and a change in the slope of some of the frequency pressure shifts.

The simultaneous changes in the x-ray diffraction and Raman scattering upon compression are interpreted as evidence for a new crystalline phase transition in α -quartz at 21 GPa [1]. With further compression, the new phase gradually pressure-amorphizes. Upon quenching, any remaining high-pressure phase transforms with considerable hysteresis to a quartz-like structure, and most likely undergoes partial decompression amorphization.

Fig. 1. (a) Interplanar spacings (d), and (b) representative energy-dispersive synchrotron x-ray diffraction spectra from quasihydrostatic compression of polycrystalline α -quartz. Open circles and Q symbols correspond to quartz diffraction, solid circles and Q' represent shifted quartz-like peaks, and solid squares and * depict new non-quartz peaks. Diffraction from neon (Ne), the pressure medium, and ruby (R) serve to calibrate pressure.

Fig. 2. Micro-Raman spectra of quartz (a-c) with increasing pressure, (d) with decompression, and (e) quenched. Maximum experimental pressure for this experiment was 24.2 GPa. The spectra were measured in backscattered geometry with 514.5-nm excitation using a Dilor XY spectrograph equipped with a CCD detector.

Direct Observation of Microscopic Inhomogeneities in High T_c Superconductors

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Structural inhomogeneities in two high-temperature superconductors have been observed within a few μm . By means of energy dispersive diffraction to 80 keV, changes in the c -axis lattice parameters of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ were detected within a spatial scale of 10 μm . These changes are interpreted as evidence of variations in the oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and in the cerium content in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$, both will affect the superconducting properties. This is the first example of directly detecting structural variations on a spatial scale of this size. The existence of such structural inhomogeneities brings into question whether exotic experimental results obtained from high T_c superconducting materials actually reflect their intrinsic properties.

Fig. 1: Variation of the oxygen parameter, $7-\delta$, and of the c -axis lattice parameter, both as a function of position, z , along the length of the crystal; scans were made at three different settings in y : circles - near the center ($y = 0.00 \mu\text{m}$); squares - closer to the lateral face ($y = 20 \mu\text{m}$); triangles - within about 6 μm of the face surface ($y = 30 \mu\text{m}$). The solid and dashed lines are intended as guides to the eye.

Fig. 2: Variation of the Ce content measured by EDXS (open circles) and of the c -axis lattice parameter as measured by energy dispersive x-ray diffraction (closed symbols).

X17C

Structural Perfection in Physisorbed Films: A Synchrotron X-ray Diffraction Study of Xenon Adsorbed on the Ag(111) Surface

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Synchrotron x-ray diffraction has developed rapidly in recent years as a technique for *in situ* monitoring of surface structure during film growth. The method has been applied to layer-by-layer growth at semiconductor^{1,2} and metal surfaces³ as well as at a metal-semiconductor interface.⁴ These experiments have exploited the extreme brilliance of synchrotron x-ray sources to obtain submonolayer sensitivity as well as high resolution in reciprocal space for precise determination of structural parameters. Unlike more surface sensitive probes, the penetrability of x-rays allows one to follow the structural evolution of the surface region from monolayer thickness to bulk and to analyze the observed diffraction patterns kinematically.

Although rare gases physisorbed on single-crystal metal surfaces offer some of the most appealing films to model theoretically, due to the simplicity of the adatom-adatom and adatom-substrate interactions, synchrotron x-ray diffraction studies of the structure and growth of these systems have lagged behind those on semiconductor and metal surfaces. We have recently used synchrotron x-ray scattering to investigate the structure and growth of xenon films physisorbed on the Ag(111) surface. For growth under quasi-equilibrium conditions, we find the bulk Xe-Xe spacing is reached at monolayer completion and fcc films of thickness $\geq 220 \text{ \AA}$ are observed. Under kinetic growth conditions, intensity oscillations at the Xe anti-Bragg position of the specular rod are observed as a function of time, indicating layer-by-layer growth.

The figure shows specular reflectivity ($00l$) scans (open circles) at 33 K for kinetically grown Xe films of nominal thickness 1, 2, 3, and 10 layers labeled A, B, C, and D, respectively. At each point, the intensity has been integrated transverse to the rod. Note logarithmic intensity scale and, on the horizontal axis, l is in units of $0.59 \text{ \AA}^{-1}$. The dashed curves are the calculated reflectivity corresponding to the nominal film thicknesses after corrections for illuminated sample area and Lorentz-polarization factor. The solid curves are best fits obtained allowing partial occupancy of the Xe layers (A, B, C) or a Gaussian distribution of thicknesses for independently scattering domains (D). The solid curves (B, C, D) yield a value of $3.55 \pm 0.1 \text{ \AA}$ for the spacing between the Ag(111) surface and the first Xe layer in agreement with previous dynamical LEED experiments.⁵

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ANOMALOUS DIFFUSE SCATTERING STUDY OF LOCAL ORDER IN SINGLE CRYSTAL $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$

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The high-Tc superconductor $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ has been an interesting material both for its potential application and its superconducting mechanism, being an electron-type rather than the more common hole-type ceramic superconductor. Two sets of data were taken near the Ce L absorption edge on a single crystal, at 5725eV and 5575eV respectively. The figure shown below is the difference x-ray intensity distribution on the HKL(L=7) reciprocal lattice plane. The difference intensity was used to simplify the analysis. The diffuse wings around Bragg peaks are anisotropic and tend to elongate toward $\langle 110 \rangle$ directions. This could mean that there is a tendency to form clusters of the same elements along $\langle 110 \rangle$ directions. Analysis is currently underway to find out whether there is short-range order on the Nd/Ce sublattice, and the resultant atomic displacement field.

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MULTIPLE BRAGG SCATTERING IN QUASICRYSTALS. IS Al-Pd-Mn CENTROSYMMETRIC?

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When a crystal is rotated around the scattering vector for a Bragg reflection P, another reflection H may be simultaneously excited for a particular value ψ of the azimuthal angle. The plot of the intensity I_P vs. ψ (called: Renninger plot) shows peaks with asymmetric features from which phases of structure factors can be obtained. Multibeam diffraction data have been obtained on high quality Al-Pd-Mn quasicrystals using synchrotron x-rays at NSLS. Rocking widths of 36 arcsecs. have been obtained, which made it possible to obtain data that could be interpreted using dynamical theory without any need of smearing functions to take into account mosaic spread. The asymmetric features and the peak intensity of a Renninger plot could be fitted with phases consistent with a non-centrosymmetric structure. This result contrasts with an earlier experiment done by one of us (M. d.B.) in which Friedel pairs were found to be identical, in agreement with a centrosymmetric structure. We are not able at this time to explain this discrepancy.

Asymmetry effect at the base of a three-beam diffraction peak in a Renninger plot. Heavy points are experimental data. The best fit is obtained with a triplet invariant δ which is not consistent with a centrosymmetric structure.

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X-18A

EFFECT OF DOPANTS ON ARSENIC PRECIPITATION IN LT-GaAs

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Over the last ten years there has been considerable research done on growing good quality films of GaAs with an MBE at low temperatures. It has been observed that it is possible to grow a non-stoichiometric GaAs film at low growth temperatures in an excess arsenic environment. The excess arsenic in these LT-GaAs films tends to cluster on annealing. This is a very unusual phenomenon for a covalent compound making it an interesting material for further study. Also, these clusters deplete the surrounding regions, making the LT-GaAs a good semi-insulating material. This allows for the development of good MESFET's (Metal Semiconductor Field Effect Transistor) with good device isolation. LT-GaAs has also been used to make photodiodes with time constants in the femtosecond range. These and other excellent device characteristics of these compounds makes this novel clustering phenomenon an interesting feature to study. The usefulness of this material in electronics also makes it essential to understand the system, so as to control the excess As-incorporation to get the best possible properties. With this in mind, high resolution x-ray diffraction using synchrotron radiation was used to characterize GaAs grown by MBE at low temperatures (200-250°C). The lattice mismatch in the LT-GaAs, which appears to be related to the amounts of excess arsenic incorporated, is observed to be different in the n-type and the p-type layers. Annealing at temperatures between 500°C and 1000°C results in a decrease in the lattice mismatch between the LT-GaAs layers and the substrate. The LT-GaAs lattice was observed to relax to the substrate lattice on annealing at temperatures greater than 700°C for 30 secs. The (0003) of the Arsenic clusters is oriented along the (111) of the GaAs matrix. There are four possible variants with this orientation relationship and all four were observed. The volume fraction of the As precipitates increases to a maximum value and remains constant on annealing at temperatures greater than 700°C, indicating that precipitate coarsening stage has been reached.

Lattice mismatch, particle Size and distribution, and volume fraction of the Arsenic precipitates as a function of annealing temperatures.

	Lattice mismatch (%)	Particle Size (Å)	Volume Fraction (%)	Particle density ($10^{16}/\text{cc}$)
As-Grown	0.151	-	-	-
500 C	0.139	-	-	-
600 C	0.093	39	1.31	5.27
700 C	0.06	68	1.69	1.28
800C	-	192	1.70	0.573

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X18-A

IN-SITU X-RAY STUDIES OF $\text{YBa}_2\text{Cu}_3\text{O}_x/\text{LaAlO}_3$ MULTI-LAYERS

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We fabricated a new sputtering cell equipped with mylar windows and multi-target sputtering guns allowing us to study the growth of multi-layer structures by in situ X-ray diffraction. In particular we examined in real time growth of $\text{YBCO}/\text{LaAlO}_3$ multi-layers. Previous studies we conducted on $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) films indicated that the c-axis orientation of YBCO always nucleates at the earliest stages of film growth, even in a-axis films. This behavior was observed in the a-axis YBCO layers of our multi-layers, indicating that the LaAlO_3 layers behave as new substrates. This could prove to be useful in the formation of S/I/S junctions. Since the YBCO layers on either side of the LaAlO_3 barrier have differing orientations, pin hole shorts in the insulating layer could be minimized by an edge junction effect.

The design of our chamber also permits grazing incidence experiments and this technique was used to study the in-plane structure of $\text{YBCO}/\text{LaAlO}_3/\text{YBCO}$ tri-layers. In the very early stages of film growth, only a-axis growth was observed. At around 300 Å, both a and c axis growth was observed. This is consistent with earlier observations where c-axis growth is observed perpendicular to the plane at the beginning of deposition, followed by a-axis dominated growth.

Recent modifications to our sputtering cell have enabled us to implement computer control of our multi-target sputtering guns. This improvement has allowed us to study the growth of $\text{YBCO}/\text{LaAlO}_3$ superlattices on SrTiO_3 substrates. We observed satellite peaks of up to sixth order in some samples. The central Bragg peak of the structure was at 45.9° (at 700°C, $\lambda=1.556\text{\AA}$). The full width at half maximum of the Bragg peak ranged from 0.05° to 0.1° . Cross-sectional TEM pictures have confirmed the periodic structure of the films.

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Structure and Growth of Hexane Films Adsorbed on the Ag(111) Surface

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Knowledge of the surface structure of organic films adsorbed on metals is fundamental to the technology of catalysis, lubrication, and adhesion. As a starting point for investigating these technologically important films, it is of interest to bring the power of synchrotron x-ray diffraction to bear on the question of the structure and growth of films of relatively short-chain hydrocarbons such as the *n*-alkane hexane [CH₃(CH₂)₄CH₃] adsorbed on the close-packed Ag(111) surface. Such experiments naturally follow our earlier investigations of the multilayer structure and growth of xenon on the Ag(111) surface.^{1,2}

Thus far we have demonstrated monolayer sensitivity by observing two Bragg reflections of a single layer of hexane on the Ag(111) surface. Coverage is determined by use of an *in situ* low-energy electron diffraction (LEED) apparatus. A step-like attenuation occurs in the Ag(10) LEED spot intensity at monolayer condensation. At higher coverages, we observe Bragg peaks which correspond to epitaxially grown bulk hexane. The (101) plane of the bulk triclinic structure is parallel to the Ag(111) surface. To follow the film growth, we show in Fig. 1 the intensity as a function of time at the anti-Bragg point ($Q = 0.858 \text{ \AA}^{-1}$) associated with the (101) reflection on the specular rod. The hexane leak valve is opened when the Ag substrate is at a temperature of 170 K establishing an ambient pressure of 1.0×10^{-8} Torr. The substrate is then cooled as the liquid hexane monolayer adsorbs. This results in a decrease in the intensity at the anti-Bragg point due to destructive interference between the monolayer and Ag substrate. Subsequently (after ~40 min), the liquid monolayer freezes ($T = 155 \text{ K}$), resulting in a further intensity decrement from the density difference between the liquid and solid monolayer. After ~60 min ($T = 130 \text{ K}$) the intensity begins to increase as a second solid hexane layer begins to grow. The second layer is complete after ~75 min ($T = 120 \text{ K}$) at which point the bare Ag reflectivity is nearly recovered. Further growth of the hexane film results, once again, in an intensity decrease at the anti-Bragg point with the intensity approaching a constant value at long times ($T = 100 \text{ K}$).

In Fig. 2, we show a specular reflectivity scan for a hexane coverage of ~4 layers estimated from the deposition time. Our preliminary interpretation is that it has a two component structure with a sharp peak at $Q = 1.72 \text{ \AA}^{-1}$ corresponding to the (101) reflection of epitaxially grown bulk hexane and a more smoothly varying component due to the hexane film.

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EXAFS STUDIES OF LIGHT INDUCED ELECTRONIC SPIN STATE TRANSITIONS IN FE(II) COMPLEXES

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The EXAFS studies for the Fe(II) complexes undergoing the spin state transition from the low spin (¹A₁) state to the high spin (⁵T₂) state are conducted for both thermally activated and light induced processes. The previous X-ray diffraction study has shown a 0.2 Å Fe-N bond elongation from a thermally activated ¹A₁ to ⁵T₂ transition in Fe(II)[α-picolyamine]₃ (Fe[pic]₃) complex. Our EXAFS results at 20K and at 290K have shown the same bond length change for the powder sample as obtained in the X-ray diffraction. The same spin state transition can be light induced at a temperature below the transition temperature, and the relaxation rate from the photoinduced ⁵T₂ back to ¹A₁ is temperature dependent. However, structural information is lacking for the light induced spin transition process. Taking advantage of the sample form flexibility, the EXAFS studies were conducted in methanol solution for the photoinduced spin transition. The EXAFS spectra of the solution at 290K and at 20K are similar to those of the powder at the same temperatures. However, illumination with a Hg lamp at 20K on the solution sample created a molecular species with a distinctively different EXAFS spectrum from those for ¹A₁ or ⁵T₂ of Fe[pic]₃ (Figs. 1 and 2). The optical spectra for the same sample in the same illumination process also show the evidence for a photoinduced intermediate distinctive from ¹A₁ or ⁵T₂. The Fe-N distances in this intermediate are close to those for ⁵T₂ despite some slight differences, but its near edge spectrum is very different from that for ⁵T₂. This is likely an intermediate with a different electronic and nuclear structure and could be an excited intermediate trapped at the low temperature. Further studies with Mössbauer spectroscopy and some quantum mechanical calculation are in progress.

Figure 1. Near edge spectra of Fe[pic]₃ in methanol solution.

Figure 2. FT EXAFS spectra of Fe[pic]₃ in methanol.

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X18B

STRUCTURE OF SUPPORTED NANOPHASE TITANIA CLUSTERS AS DETERMINED BY X-RAY ABSORPTION SPECTROSCOPY

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The materials we investigated were amorphous, high surface area, Ti-Si mixed oxides having various elemental compositions. Figure 1 shows the Fourier transforms derived from Ti K edge EXAFS of a mixed oxide and pure titania. The first shell Ti-O distance is clearly shorter in the mixed oxide than pure titania. Due to the high disorder of the solid and the presence of Si (a low Z scatterer) in the second coordination shell, the Fourier transform of the mixed oxide has little structure beyond 2 Å. In addition, analysis of the EXAFS indicates that the Ti-O coordination number also decreases with incorporation of silica into titania. The appearance of a significant pre-edge peak in the XANES of silica-rich mixed oxides is consistent with most of the Ti atoms residing at sites that have tetrahedral symmetry. A unique Ti microdomain structure in a silica-rich sample (Ti:Si 1:8) was identified by EXAFS, XANES, UV, and IR spectroscopies and is described by a single TiO₆ octahedron connected through bridging oxygens to TiO₄ tetrahedrons. X-ray absorption experiments performed *in situ* revealed that the local structure around the Ti is greatly perturbed by ambient humidity indicating that surface Ti-O-Si linkages at the domain boundaries may be easily hydrolyzed.

Figure 1. Comparison of Ti radial structure functions, not corrected for phase shifts, for Ti:Si 1:8 mixed oxide (solid line) and synthesized TiO₂ (dotted line).

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X18B

EXAFS Study of Rh and Rh+Mn²⁺ in Cages of Zeolite Y; Effects of Mn on the Location of Rh ions and the Size of Rh Clusters

G.D. Lei, H. Treviño, W.M.H. Sachtler (Northwestern U.)

Manganese promoted rhodium catalyzes the conversion of synthesis gas (CO + H₂) to oxygen containing compounds. The objective of our research is to identify the interaction of Mn²⁺ ions and Rh clusters in zeolite cages. The presence of Mn was found to affect the growth of Rh clusters, both during reduction and catalytic operation. New Rh-EXAFS data, acquired at NSLS show pronounced effects of Mn²⁺ ions on: (1) the distribution of Rh³⁺ ions over various zeolite cages after calcination of ion exchanged samples at 500°C, and (2) the size of the Rh clusters after reduction at 200°C.

As the chemical nature of the manganese (Mn²⁺ ions or MnO clusters) depends on the proton concentration in the zeolite, we also differentiate between samples prepared at a low pH of 6.5 (=LPH) and at a high pH of 11 (=HPH). Fourier transform of Rh at the K-edge are shown in Figure 1 for Rh/NaY and (Rh+Mn)/NaY(LPH) after calcination at 500°C. Clearly, back scattering from framework Si or Al is much stronger for Rh/NaY. This indicates that the Rh³⁺ ions in Rh/NaY are mainly located in hexagonal prisms, but in (Rh+Mn)/NaY(LPH) the Rh³⁺ Mn²⁺ ions compete for these sites, which leave more Rh³⁺ in sodalite or supercages, where back-scattering from Si or Al is much weaker.

After reduction at 200°C rhodium clusters are formed, their size is indicated by the peak height of the Rh-Rh scattering in the EXAFS Fourier transform. Fig. 2. shows a dramatic effect of Mn and of the pH on the size of these Rh clusters. The Rh-Rh coordination is very low in reduced Rh/NaY and (Rh+Mn)/NaY(HPH), but it is much larger for (Rh+Mn)/NaY(LPH). This indicates that Rh³⁺ ions in hexagonal prisms are hardly reduced; but when these sites are blocked by Mn²⁺ ions, the Rh³⁺ ions are located in supercages, where reduction and clustering of Rh⁰ are easy. In the HPH samples Mn is present as MnO, which does not block hexagonal prisms.

Figure 1. Fourier transform of calcined samples

Figure 2. Fourier transform of reduced samples

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A NEW "PLUG-FLOW" CATALYTIC REACTOR DESIGN FOR *in situ* X-RAY ABSORPTION SPECTROSCOPIC STUDY

Di-Jia Liu and Heinz J. Robota (AlliedSignal)

One advantage of using *in situ* X-ray absorption spectroscopy to study catalysts is that allows simultaneous measurement of the catalytic activity and structural changes. Therefore a relationship between the catalytic properties and the electronic/geometric structure can be established. One of the often encountered problems, however, is the limited quantity of the catalyst sample due to the requirement of optimum absorption path. Less catalyst will generate less product, which, in turn, makes it difficult to determine the catalytic activity. The reactor design, therefore, has to ensure an effective catalytic conversion in order to produce sufficient amount of product to be monitored simultaneously. The reactor also has to sustain repeated high temperature treatment.

To meet these requirements, we designed a special type of flow-through reactor for our XAS study. Shown in **Fig. 1** is the reactor head where the catalyst sample is located. Basically, a stainless steel AN-type female connector from Swagelok was modified and welded onto a stainless steel flow tube from which the reactant flow enters (Part 3 in **Fig. 1**). The removable sample holder consists of two parts. The center part is a tubular stainless steel holder with a male AN-type head (Part 2). This central tubular holder is held by an outer tube with matching thread to the flow tube (Part 1). A very small (0.002") gap is left between the center and outer tubes where a thin alumina filter membrane disk with >60% open volume in the form of channels is placed. During the experiment, a layer of catalyst powder which has particle size less than 100 mesh is packed into the center tube holder. The function of the alumina membrane disk is to physically hold the sample powder at the down stream side while allowing gas flow with minimum resistance. At the upstream side, a small amount of quartz wool is inserted to prevent the loosening of the powder. The whole sample holder assembly is fastened onto the female AN connector at the end of the flow tube. The flow tube assembly is centered in a quartz tube of which the catalyst section was surrounded by a resistive heating unit. Using a metal-to-metal AN-type connection, we are able to seal the junction of the in-flow tube and the sample holder and therefore to force the flowing gas through the catalyst bed without by-pass. The stainless steel construction is relatively corrosion free and thermally stable during repeated temperature treatment up to 700°C. The relatively large opening of the sample holder allows us to pack a thin layer of catalyst which is sufficient to produce detectable amounts of products. The uniformly distributed thin layer is also ideal for X-ray absorption spectroscopy.

Figure 1 The *in situ* XAS reactor head design.

By using this reactor, we have been able to increase the catalytic conversion level and therefore to enhance the sensitivity for monitoring the effluent gas. Considering that most reactions under this type of study have to be run in the "differential region", the benefit of this reactor design is significant. The long inlet tube allows the reaction gas to be preheated to reaction temperature before reaching the catalyst bed. The maximum operating temperature of the reactor is currently limited by the stainless steel parts which fuse at 850 °C and by the alumina disk which ruptures at 830 °C. This problems can be remedied by using high temperature materials.

An *in situ* CATALYTIC REACTOR SYSTEM FOR X-RAY ABSORPTION SPECTROSCOPY STUDY

Di-Jia Liu and Heinz J. Robota (AlliedSignal)

An advantage of X-ray absorption spectroscopy is that X-rays can penetrate the catalyst sample without disrupting the catalytic process. It is therefore feasible to operate a catalyst at its reaction temperature and pressure while monitoring the electronic and local structure of the catalytic elements. Recently, we designed such a reactor system for our *in situ* X-ray absorption spectroscopic study of Cu/ZSM-5 during NO catalytic decomposition. Using this reactor set-up, we have been able to monitor the NO decomposition rate while simultaneously taking EXAFS and XANES spectra.

Shown in **Fig. 1** is the schematic diagram of the reactor system. Reactor 1 is a flow-through type of reactor where NO decomposition was carried out. About 100 mg of sample is packed as a thin, permeable disk and placed in a flow-through sample holder at the center of Reactor 1 which is surrounded by an insulated resistive heater. The sample holder was designed in such a way that all the reactant flow has to pass through the catalyst, similar to a plug-flow reactor. The temperature of Reactor 1 is controlled by a programmable Eurotherm temperature controller. During *in situ* measurement, the temperature of Reactor 1 is typically in the range of 573 to 873 K. The reactant flow, 1%NO/N₂ mixture in this case, is adjusted to a flow rate of 100 ml/min by the flow controller and is directed into Reactor 1 where the decomposition reaction takes place. Under normal laboratory conditions, the conventional approaches to analyze the effluent of the decomposition products, which contain N₂, O₂, NO₂, and unreacted NO, use either gas chromatography (GC) or chemiluminescence detection of NO_x (NO_x detector). In principle, either of these approaches would be satisfactory for monitoring catalyst performance at a synchrotron. Unfortunately, such pieces of equipment are relative expensive and delicate, making them difficult to repeatedly ship and set-up within a short period on a remote site, such as a synchrotron facility.

We developed an alternative detection method. The new approach takes advantage of the well known differences in reaction kinetics between NO and O₂ (and NO₂) in the catalytic oxidation of CO over Cu based catalysts. Thus, we have substituted the production of CO₂ from the selective reaction of O₂ (and presumably any NO₂ produced through NO and O₂ reaction) with CO for the direct detection of NO related species. Schematically, the effluent from the NO decomposition reactor is mixed with a stoichiometric amount of 1%CO/N₂ mixture before entering Reactor 2 which contains a Cu,Sn/γ-Al₂O₃ catalyst, as is shown in **Fig. 1**. The temperature of Reactor 2 is controlled at 450 K throughout the experiment. Our laboratory tests showed that under these conditions, CO will react preferentially with the decomposition products O₂ and NO₂ to form CO₂ over the Cu,Sn/γ-Al₂O₃ catalyst while NO is unaffected. Our laboratory test also showed that the majority of NO₂ produced through the reaction of NO with O₂ will be decomposed back to NO and O₂ in Reactor 2 which further react with CO. Therefore, the CO₂ content represents closely the stoichiometric amount of O₂ formed. The concentration of CO₂ in the effluent is detected by a non-dispersive CO₂ infrared detector downstream of Reactor 2. Therefore, the relative NO conversion level can be monitored by the change of CO₂ content. The use of the secondary reactor and CO₂ NDIR provided us a robust, portable, yet inexpensive approach. Since it is an indirect measurement, we limited our determination of the NO decomposition data only as relative values for comparison.

Figure 1 The schematic diagram of the *in situ* XAS reactor system.

in situ CHARACTERIZATION OF Cu-ZSM-5 BY X-RAY ABSORPTION SPECTROSCOPY: XANES STUDY OF Cu DURING NO DECOMPOSITION

Di-Jia Liu and Heinz J. Robota (AlliedSignal)

Nitric oxide, NO, is one of the major constituents in air the pollutants generated by high temperature combustion devices such as automotive engines and industrial boilers. Although NO is thermodynamically unstable with respect to molecular oxygen and nitrogen, the direct decomposition reaction

is an untenable process due to the lack of a suitable catalyst. Recently, there has been many reports studying direct NO decomposition over a copper zeolite catalytic system, Cu-ZSM-5¹. Several reaction mechanisms have been proposed to explain the extraordinary catalytic activity of Cu-ZSM-5. Among them, Hall and co-workers suggested a redox reaction scheme in which the formation of Cu(I) from reductive desorption of oxygen over Cu(II) is a key step in NO decomposition². Conventional analytical techniques, such as FTIR, ESR, TPR, microbalance etc., have been applied to characterize the copper oxidation state under various conditions in order to elucidate the nature of Cu species present, these measurements were not made under actual NO decomposition reaction conditions.

Reported here is our recent *in situ* investigation of Cu in Cu-ZSM-5 by the X-ray absorption near edge structure (XANES) method at X-18B of NSLS. An advantage of X-ray absorption spectroscopy is that X-rays can penetrate the catalyst sample without disrupting the catalytic process. It is therefore feasible to operate a catalytic reaction at its *in situ* temperature and pressure while monitoring the electronic and local structure of the catalytic elements. We designed such a reactor system for NO decomposition with which we can measure the relative NO conversion level while taking EXAFS and XANES spectra. We observed that the 1s→4p electronic transition of Cu(I) in Cu-ZSM-5 appears as a narrow, intense peak, which is an effective measure of changes in the copper oxidation state during NO decomposition. This transition is quite intense after Cu-ZSM-5 is activated in inert gas flow, however, its intensity decreases after the admission of NO/N₂ gas mixture. We conducted the reaction in a temperature cycle around the optimum conversion temperature of 773 K and recorded the XANES at each temperature. We observed that the integrated intensity of the Cu(I) 1s→4p transition was strongly temperature dependent and correlated with the NO conversion level, as is shown in Fig. 1. This finding supports the conjecture by Hall et al.² and others that Cu(I) in ZSM-5 participates in the NO decomposition reaction at elevated temperature. The suppression of both the decomposition reaction and Cu(I) content by addition of oxygen in the reactant stream was also observed.

Figure 1 Cu(I) concentration correlates well with NO decomposition rate at different temperature.

¹ For example, M. Iwamoto, N. Mizuno and H. Yahiro, *Sekiyu Gakkaishi*, **34**, 375 (1991) and the references therein.

² W. K. Hall and J. Valyon, *Catal. Lett.* **15**, 311 (1992).

in situ CHARACTERIZATION OF Cu-ZSM-5 BY X-RAY ABSORPTION SPECTROSCOPY: XANES STUDY OF Cu OXIDATION STATE DURING SELECTIVE CATALYTIC REDUCTION OF NO BY HYDROCARBON

Di-Jia Liu and Heinz J. Robota (AlliedSignal)

The emission of nitrogen oxides, NO_x, has caused serious damage to terrestrial and aquatic ecosystems. Developing a catalytic system to remove NO_x at its sources is a challenging problem in environmental catalysis science. Recently, it has been shown by Held and co-workers¹ and Iwamoto and co-workers² that copper ion-exchanged ZSM-5 has high catalytic activity for removing NO_x using small amounts of hydrocarbon in an excess of oxygen. Since then there has been much debate on the role of hydrocarbon in the selective catalytic reduction of nitrogen monoxide under oxidizing conditions. Various reaction schemes have been proposed which can be summarized into the following categories; a) redox mechanism through Cu(I) which is generated by hydrocarbon reduction, b) deposition of catalytically active carbonaceous materials, and c) oxygenated hydrocarbons as reaction intermediates to further react with NO.

We investigated the mechanism of selective NO reduction by hydrocarbon by examining the Cu oxidation state change in Cu-ZSM-5 during the catalytic reaction using XANES. The XAS study was carried out at X-18B using an *in situ* reactor system which we developed recently³. We observed that even under strongly oxidizing conditions (NO/C₃H₈/O₂ = 3200ppm/3200ppm/7.5%), a significant fraction of copper ion in ZSM-5 is reduced to Cu(I) at elevated temperature when propene was present in the reactant stream. XANES spectra show a narrow peak assigned to the Cu(I) 1s→4p transition which intensity first increases with reaction temperature and then decreases when the temperature is above 640 K. By integrating the Cu(I) 1s→4p peak intensity using a normalized difference XANES method, we obtained the change of Cu(I) relative concentration with the reaction temperature, as is shown in Fig. 1(star). In the reaction mixture of NO/C₃H₈/O₂, there exists a window of cuprous ion concentration enhancement which matches quite well with the NO conversion temperature window measured by Iwamoto and co-workers². For comparison purposes, we also studied the Cu(I) concentration change in a CH₄/NO/O₂ mixture, shown as the solid squares in Fig. 1. Unlike propene, methane shows no selectivity for NO over Cu-ZSM-5. Indeed we did not observe any window of Cu(I) enhancement, rather, a monotonically increasing concentration with temperature. Our study indicates that cupric ion can be partially reduced by propene even in a strongly oxidizing environment which may be a crucial step for high NO conversion through a redox mechanism.

Figure 1 Comparison of the relative Cu(I) concentration in different gas mixtures with NO conversion level.

¹ W. Held, A. Koenig, T. Richter and L. Puppe, SAE Paper 900496 (1990).

² M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u and N. Mizuno, *Shokubai*, **33**, 430 (1990).

³ Di-Jia Liu and Heinz J. Robota, to be published in *Catal. Lett.*

STUDY THE INTERACTION BETWEEN CARBON MONOXIDE AND CUPROUS ION IN Cu-ZSM-5 BY X-RAY ABSORPTION SPECTROSCOPY

Di-Jia Liu and Heinz J. Robota (AlliedSignal)

The potential of using Cu/ZSM-5 to treat exhaust gas emission from "lean burn" automobile engine has generated interest in the environmental catalysis research area¹. One of the focal points of the research is to understand the oxidation state and geometric structure of Cu during the reaction and therefore to correlate these physical properties with the reaction mechanism.

Carbon monoxide, CO, is one of the major pollutants in the exhaust gas. It is well known in catalysis that CO interacts strongly with cuprous ion, Cu(I), but not cupric ion, Cu(II). We have recently investigated the electronic and local structure of Cu in ZSM-5 during reaction with CO by XANES and EXAFS spectroscopic methods. Interestingly, we observed that after autoreduction in inert gas, the Cu(I) local structure changes instantly when 5%CO in N₂ flow was introduced into the system at a temperature below 673 K. Analysis of the EXAFS spectrum at room temperature showed a broader 1st shell radial distribution function with a shell distance slightly increased, in comparison with that directly obtained after NO treatment. XANES also showed that the adsorption of CO on Cu(I) in ZSM-5 resulted in a sharp peak at 2 eV above the inflection point of the Cu metal edge. This peak is about 2.2 eV below the 1s→4p transition of Cu(I) in ZSM-5, indicating that charge transfer from CO to Cu(I) occurred. The strong interaction between Cu(I)/ZSM-5 and CO was further confirmed by FTIR spectroscopy at ambient temperature. The vibrational frequency of the CO stretch was found to be between the frequencies of gaseous CO and CO⁻ which indicates that the CO bond is weakened by the partial electron transfer to Cu(I). The combination of the infrared result and the 1s→4p transition energy red shift in XANES indicates that a strong p-p orbital interaction between CO and Cu(I). The CO-Cu(I) peak disappeared when the reactor temperature was raised above 673 K, presumably due to the desorption of CO. Instead, it was replaced by the 1s→4p transition of Cu(I) in ZSM-5. Exposure of a fresh or oxidized Cu-ZSM-5 catalyst to CO at room temperature yielded no reaction, indicating that Cu(II) does not react with CO as previously believed. With the increase of reaction temperature, however, CO can reduce Cu(II) to Cu(I) or Cu(0), depending on copper exchange level, reaction temperature, the reduction time, etc.

¹. See for example, M. Iwamoto, M. Furukawa and S. Kagawa, in "New Developments in Zeolite Technology", eds. Y. Murikami, A. Iijima and J. W. Ward (Elsevier, Amsterdam, 1988)

EXAFS STUDY OF BIMETALLIC CATALYSTS: Pt/Cu SUPPORTED ON ACTIVATED CARBON

Simon R. Bare, Larry N. Ito, Joe J. Maj (The Dow Chemical Company, CR&D Catalysis Laboratory, Midland, MI 48674)

Cu/Pt bimetallic catalysts supported on activated carbon have shown significant activity in chlorofluorocarbon degradation. In order to more fully understand the structure-activity relationships in these catalysts we have begun a multi-technique catalyst characterization program. We are characterizing these catalysts as a function of total weight loading, Cu/Pt ratio and pre-treatment. We have performed an initial in situ EXAFS/XANES investigation to probe the local structure of these catalysts in their freshly reduced state. The figure below shows a comparison of the unreduced and in situ reduced (250 °C in 5% H₂ in He) Cu K-edge and Pt L₃-edge XANES of a 0.5 wt % Pt / 0.9 wt % Cu on activated carbon catalyst prepared from chloride precursors. All the Pt and Cu are reduced to the metallic state by this treatment as shown by the white line intensity for Pt and edge position for Cu. The Cu K-edge and Pt L₃-edge EXAFS data are being analyzed, but initial results show that true bimetallic Cu-Pt particles are formed.

X19A

L-EDGE XANES OF ANTIMONY AND TIN OXIDES: IDENTIFICATION OF ANTIMONY OXIDATION STATE

Simon R. Bare, Gary E. Mitchell, R.G. Moore (The Dow Chemical Co., CR&D Catalysis Laboratory, Midland, MI 48674)

Mixed antimony and tin oxides are widely studied industrial catalysts for the selective oxidation of olefins. While there has been much work in defining the phase development in the Sn-Sb-O system many questions regarding the surface structure and active catalytic site remain. Key to the development of catalytic properties is the enrichment of the surface of the catalyst with multivalent antimony cations via surface segregation. Changes in the near-edge region at the L-edges have been shown to be diagnostic for many different systems. Therefore we have studied the XANES at the L-edges of Sb and Sn in a series of mixed tin-antimony oxide catalysts, together with a series of Sn and Sb reference compounds, in an attempt to further characterize these catalysts. The figure below shows the L_1 -edge of four of the reference materials: Sb_2O_3 and Sb_2S_3 where all the Sb is in the +3 oxidation state, $SbNaF_6$ where all of the Sb is in +5 oxidation state, and Sb_2O_4 where half the Sb is +3 and half +5 oxidation state. The position of the L_1 -edge is seen to be a sensitive indicator of the oxidation state of the Sb. There is a 5.0 eV shift to higher energy for the +5 oxidation state relative to the +3. Using the L_1 -edge position in this manner we have been able to determine the relative amounts of Sb^{3+} and Sb^{5+} in the catalysts as a function of the concentration of antimony.

ANTIMONY L_1 -EDGE XANES

X19A

THE FIRST HARD X-RAY MAGNETIC CIRCULAR DICHROISM EXPERIMENT ON PARAMAGNETIC BIOINORGANIC SYSTEMS

J. Chen, S.J. George, J. Christiansen, and S. P. Cramer (UC Davis), Z. H. Zhou and M. W. W. Adams (U. Georgia)

Recently, both soft and hard x-ray magnetic circular dichroism has attracted much attention because of the unique capabilities for investigating the magnetic and electronic structure of 3d transition metal and rare earth compounds. The potential importance of the x-ray magnetic circular dichroism technique extends well beyond the ferromagnetic or ferrimagnetic systems to which it has to date been applied. For these systems it has helped probe the relative spin orientation of different metals or oxidation states. Since mixed valence and mixed metal clusters are important catalysts in chemistry and biology, similar studies of paramagnetic metal centers in inorganic compounds or metalloproteins can be of great value for determining the metal cluster electronic structure and magnetic interactions.

We have measured the first Fe L-edge MCD spectra of *Pyrococcus furiosus* rubredoxin, and observed strong MCD effect (~30%). However, due to low fluorescence yield (< 0.5%), short photon penetration depth (< 1 μ m), and severe radiation damages, it is very difficult to measure more dilute protein samples using soft x-rays. The hard x-ray K-edge experiments are more feasible for dilute samples despite much weaker MCD effect (~1%). Hard x-ray experiments are also benefit from the longer beam life time and the lack of UHV requirement. In preliminary experiments, we have successfully measured Fe K-edge MCD spectra of rubredoxin (Figure 1). The Circular polarized lights were obtained by adjusting front slit up and down 0.1 mR at Fe K-edge energy. The observed ~1% MCD effect agrees with calculations. This result demonstrated that hard x-ray MCD experiments are indeed doable at X19A beamline without changing beamline optics.

Figure 1. The Fe K-edge absorption spectra taking with Right Circular Polarized (RCP) light at +6 Tesla (solid line) and -6 Tesla field (dash).

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FE EXAFS OF IDS OXIDIZED NITROGENASE

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Nitrogenase is responsible for the catalytic conversion of atmospheric dinitrogen to ammonia. This tetrameric enzyme contains two unique metal clusters containing 30 Fe and 2 Mo, linked by several S ligands. Although there is currently a crystallographic model for the nitrogenase enzyme, it is only a snapshot of the resting state. Complete characterization of the enzyme in various reduced and oxidized states is needed to gain a full understanding of the structural changes that occur during enzymatic function.

We have measured Fe K-edge EXAFS of nitrogenase oxidized with Indigodisulfonate (IDS). This oxidant will fully oxidize only one of the nitrogenase metal clusters - the 8Fe:8S P-cluster. By applying previously reported values for resting and fully oxidized protein Fe EXAFS[1], we have found evidence for an expansion in the Fe-S P-cluster. The resting enzyme gives an Fe-Fe distance of 2.62 Å while IDS results indicate a wider distance distribution, ranging from ~2.60 Å to ~2.71 Å. Since oxidized P-clusters have been implicated in enzymatic activity [2], these results could prove to be very important in deciphering the mechanism of nitrogen fixation.

Plot showing the fourier transforms of as-isolated (dotted), fully oxidized (dashed) and IDS oxidized (solid) Fe EXAFS

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Polarized XAS Studies of Fe/Pt Multilayers

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We have made polarized XAS measurements on a series of Fe/Pt multilayer (ML) films, deposited by dual source gated vapor deposition, onto Si-(111) substrates. These films are of interest as potential magneto-optic materials and as case studies in interface structure/electronic state tuning. The results of Fe-K EXAFS measurements for a Fe(9.0 Å)/Pt(4.7 Å) ML film in the $\epsilon||z$ (ϵ =polarization and z =layer stacking direction) and $\epsilon\perp z$ directions, along with those of α -Fe, are shown in figure 1. For α -Fe the A-feature corresponds to an 8-fold coordinate nn shell at 2.48 Å and the B-feature to 24-fold coordination at 4.75 Å.

A dramatic contraction of the nn distance in the ML is evidenced by the roughly 0.2 Å downward shift of the ML A-feature relative to that in α -Fe. Interestingly the resulting ML nn distance is very close to the z interplanar spacing, as determined by x-ray diffraction. The ML-A-feature is broader than that in α -Fe and is in fact not characterized by a single interatomic distance as evidenced by a deviation in the k dependence of its backtransform from that dictated by the Fe backscattering form factor. Analysis in terms of separate mid-layer and interface distances is being pursued. Comparison of the ML-A-features for the two polarizations indicates a small anisotropic expansion along the interlayer direction.

The relative amplitude of the ML B-feature is reduced relative to α -Fe, reflecting the higher disorder in the further neighbor shells in the ML material. The in-plane B-feature is more robust than in the $n||z$ results indicating better further shell correlations within the Fe-layers than along the layering direction.

Figure 1. The Fourier transform of the $k \chi(k)$ EXAFS oscillations above the Fe-K edge for α -Fe and two beam polarizations for a ML Fe/Pt film.

XANES STUDIES OF PHOTOCHEMICAL DEGRADATION OF URANYL CITRATE COMPLEX.

C.J. Dodge, A.J. Francis (BNL), and F. Lu (U. Kentucky)

Citric acid, a naturally occurring organic complexing agent, forms stable, water-soluble complexes with transition metals and actinides, and may involve formation of bidentate, tridentate, binuclear, or polynuclear complex species. Uranyl citrate, a binuclear complex, is photochemically degraded to acetic acid, carbon dioxide, water, and precipitation of uranium. The uranyl U(VI) ion was reduced to uranous U(IV) ion and was subsequently reoxidized to the hexavalent form. The initial pH and the presence of oxygen affected the rate and extent of photochemical degradation of the complex, the formation of intermediate organic degradation products, and uranium speciation¹. The oxidation state of the uranium in the precipitate was determined by X-ray absorption near-edge spectroscopy (XANES) using beam line X-19A. The precipitate was mounted on the conductive side of a Mylar foil and the absorption measured at the M_γ (3d-→5f) absorption peak using an electron yield detector and a double crystal Si(111) monochromator. The spectrum was normalized after background subtraction. Curve fitting using a least squares program was accomplished using one peak for the symmetrical uranium dioxide spectrum and two peaks for both the uranium trioxide and the precipitate. Uranium dioxide had a peak absorption energy of 3550.4 eV. The hexavalent uranium trioxide and the precipitate exhibited an identical shift of the primary peak to higher energy at 3551.1 eV, confirming that the precipitate contains hexavalent uranium. The second peak (shoulder) on the high energy side of the absorption peak for uranium trioxide and precipitate (2-4 eV above the maximum peak energy) is characteristic for hexavalent uranium and is due to multielectron excitations from covalent O-U-O bonding.

A process has been developed for recovery of uranium by photochemical degradation of citric acid extracts for environmental restoration of uranium contaminated soils, sludges, and wastes².

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Formation and Diagenesis of Macromolecular Organic Sulfur in Peru Margin Sediments

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Recent studies have indicated that early diagenetic reactions within sediments lead to the incorporation of sulfur into organic matter. It has been proposed that this process of "natural sulfurization" can (a) promote the preservation of labile biological molecules, and (b) subsequently influence the timing of petroleum generation from sulfur-rich source rock kerogens. Specifically, cross-linking reactions involving sulfur have been suggested as one pathway for the formation of kerogen and related macromolecules. With continued burial the dissociation of these sulfur linkages at relatively low levels of thermal stress gives rise to the apparent "early" generation of petroleum. The overall goal of this study is to develop structural models which provide a molecular-level understanding of the origin and fate of organically-bound sulfur.

Sediment samples from the Peru margin were selected for detailed study because of their high organic carbon and organic sulfur contents (TOC > 10%; S_{org} up to 10%), and because of the perception of these sediments as a modern immature analogue of Monterey Formation and other sulfur-rich source rocks. The organic sulfur geochemistry of these sediments was compared with that of consolidated sulfur-rich sediments (including the Monterey Fm.). Gross chemical (X-ray absorption spectroscopy, elemental analysis) and molecular-level (flash pyrolysis, sulfur-selective chemolysis) characterization was conducted on molecular-size fractions isolated by gel permeation chromatography in addition to total solvent extracts and kerogens. In this way, information is derived for each molecular size range concerning the organic sulfur content, the type of sulfur-containing organic molecules (i.e. chain-length, carbon skeleton), and the type (e.g. thiophenic vs sulfidic, mono vs di or polysulfide) and number of sulfur linkages.

Preliminary analyses for Peru margin samples indicate that, although sulfur incorporation takes place throughout the depth interval sampled (ca. 100m), the majority occurs in the upper few metres of sediment. Organic sulfides dominate over thiophenic sulfur throughout this sedimentary sequence. These results contrast with those from consolidated sediments where thiophenic sulfur equals or exceeds organic sulfide. These observations are in agreement with the current concepts of aromatization of cyclic sulfides during diagenesis and maturation. Comparison of kerogen/bitumen pairs and molecular size fractions from the selected samples revealed lower thiophene/sulfide ratios for high-molecular-weight fractions compared to low-molecular-weight fractions, consistent with an increase in the degree of sulfide cross-linking with increasing molecular size.

TB EXAFS

M.M. Grush (UC Davis), R. Bradly (Arizona State U), W. Frasch (Arizona State U), J. Christiansen (UC Davis), S.P. Cramer (UC Davis / ALS)

The so called oxygen-evolving complex (OEC) associated with Photosystem II (PSII) in green plants and cyanobacteria is responsible for linking the 4 electron oxidation of water with 1 electron light-induced reduction processes. Although calcium has been shown to be a necessary cofactor for oxygen evolution, some confusion remains with regards to where the calcium binding site is located.

We have been studying PSII preparations which have Tb^{3+} substituted for Ca^{2+} . The greater scattering ability of Tb, with respect to that of Ca, should make it clear whether or not there is a calcium binding site close to the Mn tetramer. Preliminary data analysis of Mn EXAFS on a Tb-substituted PSII sample requires a Mn-Tb shell at ~ 3.1 Å in order to obtain a good fit. This indicates the presence of a calcium binding site in close proximity to the Mn cluster.

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SULFUR SPECIATION STUDIES BY SULFUR K-EDGE XANES SPECTROSCOPY ON X-19A

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Sulfur K-edge XANES spectroscopy has been shown to be an excellent technique for quantitative speciation of sulfur in fossil fuels. Earlier studies focused on establishing the method and applying it to sulfur speciation in coal.⁽¹⁻³⁾ More recently, we have applied it to a variety of additional problems, including coal desulfurization,^(4,5) and speciation of sulfur in other materials^(6,8) such as asphalts and rubber.

Desulfurization processes investigated include coal treatment with boiling perchloroethylene (PCE), with single electron transfer (SET) and basic reagents, by molten caustic leaching (Gravimelt process), and by biological methods. The results indicate that the PCE method removes only elemental sulfur from coal and does not affect organic sulfur. SET and basic reagents developed by Stock and coworkers, on the other hand, do appear to remove thiophenic and sulfidic sulfur, respectively. The Gravimelt process, developed by TRW, removes most of the ash and sulfur in coal (80-90%); XANES shows that all pyritic and sulfidic sulfur, and most of the thiophenic sulfur is removed, leaving only small amounts of elemental, sulfatic, and thiophenic sulfur in the treated coal. Biological desulfurization has proven successful in removing both organic sulfide and thiophenic sulfur in at least one case.

The sulfur forms in a suite of asphalts were determined. Thiophenic sulfur varied from 54% to 78% of the total sulfur, with the balance being primarily sulfidic. The sulfidic sulfur is oxidized to sulfoxides, degrading asphalt performance. XANES results for rubber tread material used for tires identify polysulfides as the major sulfur component, followed by sulfides and thiophenes. The behavior of these sulfur forms during conversion of rubber to oil using coal liquefaction technology is now being investigated.

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X-RAY ABSORPTION MEASUREMENTS ON ION-BEAM-MIXED Pd-Ag FILMS

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Evaporated Pd/Ag multi-layered thin films were ion beam mixed to produce intermetallic alloys. In order to study the local density of unfilled 4d states of Pd, we measured the Pd L_3 edge XANES spectra of these materials.

In Figure 1, we show the Pd L_3 spectra of; pure Pd, a bulk Pd₂₅Ag₇₅ alloy, mixed and unmixed Pd₂₅Ag₇₅ multi-layered films. We note a number of points regarding these spectra. First, the unmixed-layered Pd-Ag film spectrum is identical to that of pure Pd. Second, the mixed film shows a distinct decrease in the "white line" (WL) strength compared to pure Pd. Third, the near-edge structure (beyond the WL) for the mixed film is clearly different than for pure Pd but essentially the same as for bulk Pd₂₅Ag₇₅. Since such post WL features are known to be related to the local atomic environment, we infer that the local geometrical structure of this mixed film is different from elemental Pd and essentially the same as the bulk alloy.

In Figure 2 we show the the L_3 spectra for a series of ion-beam-mixed, multi-layer Pd_{1-x}Ag_x thin films. The strength of the WL feature reduces dramatically, from pure Pd, with increasing Ag content (consistent with point two above.) This implies that the density of unoccupied Pd states with d-symmetry is reduced upon alloy formation with Ag. This charge transfer to Pd is consistent with the larger electronegativity of Pd (2.2) [relative to Ag (1.9)] and may contribute to partial filling of Pd d-band. These results can be interpreted on the basis of the charge-compensation model however, we can not rule out the intra-atomic charge transfer between Pd s and d.

Figure 1. Comparison of the Pd L_3 spectra of multilayer and ion-mixed films to bulk materials.

Figure 2. The Pd L_3 spectra of a series of ion-beam-mixed Pd-Ag films.

EXAFS Studies of Partial Methoxy Substituents of Iron(III)oxychloride

Jun-Kun Kang, Y. Jeon (Jeonju Univ. Korea), Mark Croft (Rutgers Univ.)

FeOCl has the layered structure similar to γ -FeOOH and belongs to the orthorhombic space group, Pmm with $a=3.780\text{\AA}$, $b=7.917\text{\AA}$, $c=3.302\text{\AA}$ and $Z=2$. The outer-most atoms of each layer are chlorines that are bridged with neighboring Fe atoms and run along the c axis. An oxygen atom is connected to four oxygens and two chlorines. The surface chlorine atoms can be exchangeable by other organic or inorganic anions provided the substitution would not produce strong lattice distortion.

We have prepared a series of partial methoxy substituents of FeOCl, FeOCl_{1-x}(OCH₃)_x with $x=0.1, 0.2, 0.3, 0.6, 0.8$. In contrast to pristine FeOCl, the substituents with $x < 0.25$ can intercalate alkanols into their interlayer spaces whereas those with $x > 0.25$ do not react even with amines. Such physical-chemical changes are considered to be mainly due to the structural variation of the FeOCl host upon partial methoxy substitution. In order to study structural changes, Fe K-edge EXAFS spectra were obtained in transmission mode for FeOCl and its methoxy substituents. Figure 1 shows radial distribution function of Fe in the samples. As the content of methoxy group increases; the Fe-O distance has increased by about 0.11 $\text{\AA}$, the Fe-Fe bond increases along the a -axis by 0.02 $\text{\AA}$, and the Fe-Cl bond along c -axis does by 0.05 $\text{\AA}$. Due to the replacement of Cl atoms by methoxy groups, the intensities corresponding to Fe-Cl bonds gradually decreases and the coordination of Fe-O increases upon the substitution. The intensity due to Fe-Fe bond has increased abnormally, which might be explained if Na⁺ ions are considered to be coordinated additionally to Fe atom in the substituents. [This work is support in part by PLS and KOSEF.]

EXAFS STUDY ON NANOCRYSTALLINE ZIRCONIA AND YTTRIA

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Nanostructured materials consist of two distinct structural components: crystalline grains and disordered interfacial regions containing up to 40 % of the atoms with about 85 % density compared to the bulk material¹. Typical dimensions of nanostructured materials are grain diameters of 10 nm and grain boundary thicknesses of 1 nm. Knowledge of the atomic arrangements in the interfacial regions is not only important for the basic understanding of the structure of these novel materials but also for the interpretation of interesting properties such as plastic deformation at temperatures below half of the melting point².

Nanostructured zirconia and yttria were prepared by the gas condensation method. Powders as well as bulk samples of these materials were used for EXAFS measurements and compared to materials with conventional grain size (ca. 1 μm). We did EXAFS measurements on monoclinic, orthorhombic and cubic zirconia with conventional grain size as powder. Monoclinic ZrO_2 was also investigated as bulk sample, i.e. compacted and sintered. Nanostructured ZrO_2 was measured in form of powder as well as bulk samples. Conventional yttria was investigated as powder and bulk, nanostructured Y_2O_3 was used in form of powder. EXAFS measurements were done at liquid nitrogen temperature.

EXAFS oscillations and the $\text{FT}(\chi k^3)$ in nano zirconia powder (ca. 15 nm) are distinctly weaker compared to coarse grained samples (Fig. 1). This result agrees with the idea that nanocrystalline materials consist of an ordered crystalline component and a grain boundary component with a random arrangement of atoms³. EXAFS of the nano bulk sample (80 nm) is nearly identical to the monoclinic coarse grained powder. However, due to the grain size of 80 nm the fraction of interfacial regions is low. Future experiments on fully dense nanostructured samples (grain sizes below 10 nm) prepared by hot-pressing are required to determine the interfacial contribution. A hot pressing unit to prepare such samples is near completion.

XRD analysis of the nano powders show two different crystallographic modifications of zirconia: the ambient pressure modification and a high pressure modification. These metastable high pressure modifications are not present in the bulk samples. Fitting the Fourier filtered and back transformed "oxygen peak" we can distinguish between the smaller distance (2.16 Å) in the seven fold coordinated monoclinic part and the bigger distance (2.23 Å) of the eight fold coordinated tetragonal part of the powder (Fig. 2). The calculated ratio of these two parts from the fitted EXAFS data correspond satisfying with XRD results.

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XAS STUDIES OF CHLORIDE ON ALUMINUM

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It is well known that aluminum and other passive metals undergo pitting in chloride solutions, but there is relatively little quantitative information on the interaction of oxide films with chloride ions. In the case of aluminum, the uptake of chloride ions by the passive film has been studied by X-ray photoelectron spectroscopy, radiotracer techniques, and by adsorption from solution onto powders. The present work has studied the uptake of chloride ions by oxide-covered aluminum using X-ray absorption spectroscopy and synchrotron radiation.

The X-ray absorption measurements were carried out on beamline X19A at the National Synchrotron Light Source at Brookhaven National Laboratory. Aluminum samples were foils emerged from solution under potential control after specified immersion times.

Figure 1 shows an X-ray absorption spectrum for aluminum sample immersed in deaerated 0.1 M NaCl and polarized at -0.750 V. vs. S. C. E. for one hour, i. e., just below the pitting potential ($E_{\text{pit}} = -0.700$ V. vs. S. C. E.). The X-ray edge for chlorine (i.e., chloride) occurs at the same energy both for the aluminum sample and for an NaCl standard. The X-ray absorption near edge structure (XANES) is very similar for both chloride on aluminum and for the NaCl standard. These results clearly show that chloride ions are incorporated into the oxide film on aluminum at electrode potentials prior to the pitting potential.

Using a deconvolution method, various spectra as in Figure 1 can be resolved into contributions from (i) surface chloride, (ii) bulk chloride (i. e., chloride in the oxide film), and (iii) Cl-O interactions.

These measurements are believed to be the first using X-ray absorption spectroscopy to demonstrate the uptake of chloride ions by passive films prior to localized breakdown of the passive film.

Fig. 1. XAS spectrum of chloride on aluminum at -0.750 V_{SCE} in de-aerated 0.1 M NaCl.

EXAFS Studies of Zinc Hydroporphyrins

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Interest in understanding photosynthesis, the conversion of light into a chemical energy has lead to the synthesis of a variety of mutants to the protein and chromophores in photosynthetic reaction centers. The initial step in this process is the one electron reduction of a bacteriochlorophyll (BChl) dimer. In order to better understand the role of the chromophores in this process substitution of the magnesium in bacteriochlorophyll with zinc or nickel will enable the intermediate structure to be probed via EXAFS experiments. In these studies we have investigated the structural and coordination chemistry of zinc porphyrins and substituted chlorophylls (pheophorbide-a) using EXAFS spectroscopy. From x-ray crystallography it is known that the Mg BChl's are five coordinate, with one axial histidine. From optical experiments Zn is known to readily coordinate an axial base to become five coordinate. From x-ray absorption near edge studies we observe changes in the pre-edge region which might be associated with the coordination of an axial ligands. From the edges one can clearly see a difference between the four and five coordinate complexes. However, unlike nickel the pre-edge peak intensity is apparently not attenuated upon coordination of axial ligands along the z axis, but the separation between the pre-edge and the edge decreases upon coordination of axial ligands, see Figure, for both zinc(II) porphyrin and pheophorbide-a. Analysis of the EXAFS data is ambiguous as to the coordination of the Zn, but there is an increase in the Zn-N distance by 0.03 Å upon addition of piperidine, a nitrogenous base. From these studies it is clear that experiments of zinc substituted reaction centers it will be hard to determine the coordination environment of the metal, one might be able to use the separation between the edge and pre-edge. The reason that we are unable to observe the axial nitrogen is unknown (similar results were found in studies of other zinc complexes) but it might be a result of Zn(II) being a closed shell d^{10} system.

Figure. Derivative edge plots of (a) Zn porphyrin and (b) pheophorbide at 110K with (dash line) and without (solid line) piperidine.

EXAFS Studies of Ni(II) and Ni(I) F430 and Binding of Axial Ligands

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Coenzyme M methyl reductase catalyzes the final steps in the reduction of carbon dioxide to methane in methanogenic bacteria. This terminal step is the reduction of methyl coenzyme M to give methane and coenzyme M in which factor 430 (F430), a nickel tetrapyrrole cofactor, is an essential component. F430 can be reduced to Ni(I) in vitro and in vivo and is proposed as a transient in the catalytic reaction. Isolated F430 is thermally unstable and epimerizes to the 12,13-diepimer. Both isomers have been shown to form Ni(I) complexes upon one electron reduction from optical and EPR experiments. EXAFS studies of the Ni(I) F430M and other Ni(I) complexes show two sets of Ni-N distances. The Ni(II) forms show different ligand binding affinities which has been attributed to the stability of the four coordinate species. We report here the first structural information for the Ni(I) 12,13-diepimer F430 PBA along with ligand binding studies for the Ni(II) and Ni(I).

XANES studies show a 3eV decrease in the edge energy upon reduction of the metal and an attenuation of the pre-edge peak upon coordination of axial ligands. Analysis of the EXAFS data for F430 and the 12,13-diepimer indicate that they undergo similar distortions upon reduction to Ni(I) resulting in two sets of long and short Ni-N distances. XANES and EXAFS studies of Ni(II) and Ni(I) F430 at low temperatures confirm that Ni(II) binds two and Ni(I) binds one axial ligand to form six and five coordinate species, respectively (see Figures). The six coordinate Ni(II) is high spin with Ni-N distances of 2.06 Å. The five coordinate Ni(I) has an overall increase in all of the Ni-N distances of ~ 0.05 Å. EPR and optical experiments are insensitive to coordination of ligands to Ni(I) F430.

EXAFS Studies of Cu(II) and Cu(I) Octaethylisobacteriochlorin

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The chemistry of nickel hydroporphyrins is of current interest as models for methyl-coenzyme reductase which contains the nickel coenzyme, factor 430 (F430), as its prosthetic group. This enzyme catalyzes the final step in the reduction of CO₂ to methane in methanogenic bacteria. It has been shown that nickel(II) octaethylisobacteriochlorin (OEiBC) is a satisfactory model for F430: the Ni(II) can be reduced by one electron to Ni(I) and it catalyzes the reduction of methyl iodide to methane. We present here the structural consequences of replacing Cu(II) for Ni(II) in models for F430. For Ni(I)OEiBC we have previously shown that two sets of Ni-N distances are observed whereas for copper(II), which is isoelectronic with Ni(I), only one Cu-N distance is observed at 2.0 Å. Reduction of Cu(II) to Cu(I) results in a 3eV decrease in the edge energy, Figure 1.

Fourier transforms of the k^3 weighted EXAFS for Cu(I) OEiBC with and without a crown ether (CE) are shown in Figure 2. The Cu(I) OEiBC was generated using sodium amalgam in THF; the CE is used to sequester sodium ions. Note that without CE there is a large second shell peak which is not present with CE. The presence of sodium ions near the copper (~3.0 Å) could explain the resonance Raman data for the Cu(I) OEiBC which shows a large structural change around the copper upon reduction and the decreased reactivity relative to other Cu(I) complexes and Ni(I)OEiBC, the Na atoms protect the Cu from axial attack.

Figure 1.

Figure 2.

Polarized XAS Measurements on Laser Deposited High-T_c Films

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In the past five years dramatic strides have been made in the fabrication of high quality, epitaxial, laser deposited (LD) high-T_c films for both pure and applied work. Recently attention has focused on fundamental questions in La_{2-x}Sr_xCuO₄ epitaxial films. We have used polarized Cu-K XAS (near edge and EXAFS) measurements to characterize such a LD film on a SrTiO₃ substrate. Here the relative orientation of ϵ (the x-ray polarization vector) and c (the normal to the CuO₂ planes) determines whether in/out-of plane electronic states and atomic coordinations are probed by the XAS.

Several points should be noted regarding the polarized near edge results shown in figure 1. The sharpness of the polarized spectra are as good or better than any bulk single crystal results reported in the literature. This attests to both the film quality and to the potential of using LD to fabricate high quality samples for spectroscopy. The σ and π labels in the figure 1 refer to the in (out-of) plane Cu-4p final states and the asterisk indicates the ligand hole $d_{n+1}^{\perp}$ state ($\perp$ = ligand hole and $n = 9$).

In figure 2 the results of polarized EXAFS studies on this sample emphasize the strong atomic anisotropy of this epitaxial film. The O(1) feature (appearing in the $\epsilon_{\parallel c}$ spectrum only) is associated with the close four fold Cu-O(1) coordination in the CuO₂ planes. By contrast the longer two fold apical Cu-O(2) coordination appears only in the $\epsilon_{\perp c}$ spectrum.

Figure 1. Polarized Cu-K near edges of a LD film of La_{1.85}Sr_{0.15}CuO₄.

Figure 2. Polarized Cu-K EXAFS results for the same film.

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XAS Studies of Compounds of *s/p*-Orbital (Group IIIA–VIIA) Elements

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The success of $L_{2,3}$ -edge XAS in reflecting transition metal *d* orbital electronic structure motivates the extension of similar techniques to Group IIIA–VIIA elements where the *p*-orbital occupation is crucial. Accordingly, L_1 , L_3 and *K* edge x-ray absorption studies have been carried out on compounds of *s/p*-orbital elements namely *S*, *Cl*, *Ga–Br*, *In–I*, *Tl–Bi*. We have probed the relation between the *s/p*-orbital occupancies of these elements and ‘white line’ (WL) features in their L_1 and *K*-edge spectra using L_3 -edge spectra to estimate the background continuum onset. In the same materials we have also correlated the edge energy shifts and the *s/p*-orbital occupancies.

Our results on the *K* and L_1 edges of the compounds of Group IIIA–VIIA elements show a clear correlation between the WL feature areas of these spectra and the *s/p* orbital occupancies. The L_1 or *K* edges of selected *I*, *S*, *Cl* based materials with various formal valences are shown below. The WL feature area increase with an increasing valence is clearly seen from these spectra. It should be noted that the WL area variations observed, evidence both a *p*-hole count and a transition matrix coupling variation with valence. The clear shift of the edge to higher energy in the spectra of these elements with increasing valence also reflects the shift-valence correlation we have observed.

XAS of L_1 edge of I_2 , KIO_3 and *K* edge of *S* and *Cl* compounds

XAS Studies of Molybdenum Oxides

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Several properties of *Mo* compounds have made them an attractive proving ground for fundamental studies: the variable *Mo d*-occupancy/valence state; the ability to form linear , two and three dimensional arrays of *Mo–O* complexes; and the ability to insert different doping atoms into these compounds. We have used L_1 and $L_{2,3}$ XAS to probe the *d*-orbital electronic structure of a wide range of interesting molybdenum oxide based materials.

The ‘white line’ WL features at the *Mo–L*_{2,3}-edges have been observed to reflect both the local coordination symmetry (through the *d*-crystal field structure) and the *d*-orbital occupancy in these materials. Figure 1 shows the *Mo–L*₃ spectra for a series of octahedral *Mo*-oxide compounds. The relative intensities of the low (high) energy WL-features reflect relative degeneracies of the sixfold- t_{2g} (fourfold- e_g) levels with which they are associated. The lower *Mo*-valence material (MoO_2) exhibits an intensity decrease in the t_{2g} -feature due to band filling. By contrast in figure 2 the reversed relative intensities of the WL-features reflect the tetrahedral symmetry of these materials in which the more degenerate t_{2g} level now lies above the e_g . The energy splitting between t_{2g} and e_g levels have been observed to be larger for octahedral than for tetrahedral symmetry environment as expected.

Fig. 1 *Mo–L*₃ edge spectra for a series of octahedral *Mo* compounds. (The MoO_2 spectra was shifted for alignment)

Fig. 2 *Mo–L*₃ edge spectra for a series of tetrahedral *Mo* compounds.

In-situ XAFS spectroscopic investigation of coal mineral transformations during combustion

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Inorganic mineral impurities in coal, by fouling and slagging, affect the efficiency and the performance of the combustion systems. XAFS spectroscopy is an ideal tool to investigate the reactions of coal minerals during combustion.

A schematic diagram of the furnace system built for these experiments is shown. The drop tube furnace is designed for one standard cubic foot per minute (scfm) total gas flow and one to 10 g/min of reactant feed rate at furnace wall temperatures up to 1800 K. The input gas can be a mixture of gases to produce varying oxidizing/reducing combustion conditions. The diffuser, at the top of the furnace, is designed to thoroughly mix the primary and feeder air and to distribute the solid particles uniformly across the entire flow cross sections in the alumina retort of the furnace. 2.5 sec residence time in the furnace is sufficient to achieve complete combustion of utility grind coal particles. A conical ceramic venturi at the exit of the furnace reduces the outlet gas stream diameter from 3 in. to 1 in. diameter before it enters the six-way cross. A one mm. dia. X-ray beam passes the center of the cross perpendicular to the ash stream. On a water cooled port, a solid state X-ray detector with 0.003 inch thick beryllium window is mounted, orthogonal to both the X-ray beam and the ash stream. Helium gas is purged through the X-ray inlet and exit ports as well as the detector port toward the center of the cross to reduce x-ray attenuation and to inhibit fly ash particles from flowing outward toward windows. A port across from the detector port is used for an ash deposition probe. A boron nitride (BN) disk is placed at 45 degrees to all major axes (X-ray beam, ash stream and detector) to optimize both the ash deposit collection efficiency and the X-ray signal.

In initial studies using this system, Fe K-edge spectra have been obtained from deposits during formation. To date, a pure pyrite feed, a coal refuse sample, and a Kentucky # 9 coal have been investigated. The spectra that are currently being analyzed, indicate an iron oxide-sulfide mixture.

X-RAY STANDING WAVE INVESTIGATION OF Na/Cu(111)

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We have carried out Normal Incidence X-Ray Standing Wave measurements to study the adsorbate-substrate bond length for the system Na/Cu(111). For a half monolayer of Na on Cu(111), we found the Na-Cu spacing to be $2.45 \pm 0.05 \text{ \AA}$. Increasing the Na coverage to one monolayer, our results showed the Na-Cu bond length to be $2.56 \text{ \AA} \pm 0.06 \text{ \AA}$ (see figures below). The reduction in the coherent fraction from half monolayer to one monolayer suggests a single site of Na on Cu(111) for half layer and more than one site at saturation coverage. Compared with our LEED observation for one monolayer Na on Cu(111) [(3/2x3/2)], we suggest a 50-50 mixture of top and bridge sites of Na on Cu(111) at saturation coverage.

990 eV Na KLL Auger XSW Data, 2.975 KEV

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X19A

SULFONIC ACIDS: UBIQUITOUS OCCURRENCE OF A NOVEL CLASS OF SEDIMENTARY ORGANIC SULFUR COMPOUNDS.

Vairavamurthy, A., W. Zhou and B. Manowitz (BNL)

A wide variety of organic sulfur compounds occur in sediments, resulting from the reactions of the various sulfur nucleophiles with organic molecules, and the subsequent chemical and microbial transformations of the initially present organic sulfur compounds. In past studies, which mainly used chromatographic techniques for sulfur speciation, the major classes of organic sulfur compounds identified in sediments and in petroleum include, thiols, organic sulfides, disulfides, polysulfides, and thiophene derivatives. We studied sulfur speciation in sediments from a variety of organic-rich locations (e.g. salt marsh sediments from Sheltor Island, Long Island) using sulfur K-edge x-ray absorption near-edge structure spectroscopy (XANES) which allows simultaneous determination of all the major forms of sulfur in a sample. Our results show, for the first time, ubiquitous occurrence of sulfonic acids, which constitute about 20-40% of the total organic sulfur in near-surface sediments (Figure 1). The chemical structures of the organic groups of the sedimentary sulfonic acids are not clearly understood; however, it appears that these molecules contain predominantly high-molecular weight organic moieties because they do not lend for methanol/toluene extraction. The geochemical significance of sulfonic acids in sediments is not clearly understood. Potential geochemical roles of sulfonic acids can include: (1) enhancing the preservation of sedimentary organic matter because of their potential antibacterial effects (lignosulfonates, for example, have known antibacterial properties), (2) undergoing reduction to sulfhydryl groups during late diagenesis, and its effect in increasing macromolecular complexity through disulfide cross-linking towards forming kerogen, and (3) aiding in the expulsion of oil from source rocks because of their surfactant properties.

Figure 1: Distribution of sulfonic acids in relation to other major organic sulfur forms in salt marsh sediments (Sheltor Island, New York). Solid symbols - analysis of whole sediments; open symbols - analysis of samples extracted by methanol followed by toluene.

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X19A

SULFOXYLATE ION: OBSERVATION OF A NOVEL INTERMEDIATE IN THE OXIDATION OF AQUEOUS HYDROGEN SULFIDE.

Vairavamurthy, A., W. Zhou and B. Manowitz (BNL)

X-ray absorption near-edge structure (XANES) spectroscopy has been used to detect a novel sulfide-oxidation intermediate with sulfur oxidation state of +2, that has been observed as a transient species in the Ni^{2+} catalyzed oxidation of aqueous hydrogen sulfide. Previously known intermediates species in the H_2S oxidation include elemental sulfur (oxidation state 0), polysulfides (outer sulfur: -1, inner sulfur: 0), sulfite (+4) and thiosulfate (outer sulfur: -1, inner sulfur: +5). Although oxoacid/oxoanion species with stoichiometry H_2SO_2 and HSO_2^- have previously been proposed, such an intermediate with a +2 oxidation state sulfur has never been detected experimentally. Figure 1 shows the XANES spectra of 0.1 M sulfide in deionized water (1A), and with added Fe(II) (1B) and Ni(II) (1C) after different periods of exposure to air. An unusual feature in the Ni(II) series is the presence of a peak at 2476.1 eV in the spectra of the initial oxidation period. An important advantage of using XANES spectroscopy for sulfur speciation is that the peak energy can be correlated with a sulfur oxidation state, especially for oxoanions of sulfur. This peak energy correlation provides a sulfur oxidation state of +2 for the transient intermediate. Further characterization of the intermediate was achieved using Fourier-transform-infrared (FT-IR) spectroscopy, which suggests a sulfoxylate ion (SO_2^{2-}) structure for this intermediate. The sulfoxylate ion is the lowest end member in the homologous series of sulfur oxoanions which include sulfite and sulfate. The observation of the sulfoxylate ion intermediate presents an important step forward in unraveling the mechanism of sulfide oxidation, which is still not clearly understood.

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THE PRODUCTS FROM THE OXIDATION OF AQUEOUS HYDROGEN SULFIDE BY HYDROGEN PEROXIDE.

Vairavamurthy, A., W. Zhou and B. Manowitz (BNL)

Hydrogen peroxide is a potential oxidant for mitigating the deleterious effects of hydrogen sulfide in environmental and industrial pollution control applications. In very early studies of the reaction of H_2O_2 with H_2S , elemental sulfur was described to be the main product under acidic conditions, whereas sulfate was the only product observed under basic conditions. Hoffmann (*Environ. Sci. Technol.*, 11, 61-66, 1977) studied the reaction under acidic and neutral conditions, and found both elemental sulfur and sulfate as end products, but observed the transient existence of polysulfide intermediates. Hoffmann proposed the initial formation of a HSOH intermediate that can react with SH^- to form polysulfides. However, Luther (In: *Aquatic Chemical Kinetics*, Ed.: W. Stumm, pp 173-198, Wiley, 1990) argued that such a mechanism may not be favored for the formation of polysulfides because it involves the formation of a weak S-S bond at the expense of a strong S-O bond. In an attempt to better understand the mechanism of H_2S oxidation by H_2O_2 , we used sulfur K-edge XANES spectroscopy to examine the transient intermediates. Experiments were conducted with 50 mM NaHS and varied concentrations of H_2O_2 at basic pH (ca. 12) and 25 °C. Figure 1 shows the XANES spectra at three different levels of H_2O_2 . These spectra were obtained after ca. 2 min of mixing the reagents because the reaction was almost complete within two minutes as indicated in a time-series experiment. With a five-fold excess H_2O_2 (243 mM), the products observed were: elemental sulfur (21%), polysulfides (46%), thiosulfate (7%) and sulfate (26%). However, with the minimum added level of H_2O_2 , the existence of the sulfoxylate ion (the lowest end member in the sulfur oxoanion series with sulfur in the +2 oxidation state) was observed, suggesting that H_2S oxidation by H_2O_2 proceeds through this intermediate. These results provide strong evidence that sulfoxylate ion is a common and initial intermediate in the oxidation of H_2S by both O_2 and H_2O_2 .

Figure 1. XANES spectra of NaHS- H_2O_2 reaction mixture with varied H_2O_2 levels. A: 48.5 mM; B: 97 mM; C: 243 mM.

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NEXAFS STUDIES OF POLYMER/POTASSIUM SALT COMPLEXES

X. Q. Yang, H. S. Lee and J. McBreen (BNL), F. Lu (Univ. of Kentucky)

Poly(ethylene oxide) (PEO)/salt complexes are an important new class of electrolytes. The polymer solvent, although immobile in the macroscopic sense, plays a very important role in the conduction process through local chain flexibility. Conductivity also depends on ion pairing, the formation of aggregated species, coulombic interactions among ionic carriers and interactions of the ions with the host polymer. So far we have very little information on these aspects. NEXAFS at the potassium K-edge was used to study the effects of temperature and plasticizer additions on ion pairing. The NEXAFS spectrum depends on bonding, valence, and the coordination symmetry of the potassium atoms in the sample. Data from several reference compounds showed that a splitting of the NEXAFS white line was a clear signature for ion pairing. When the K^+ ions were dissociated and complexed with the ether oxygens of PEO the white line was a single broad peak. The fine structure of the white line was used as a measure of ion pairing of an organo-potassium salt in a modified carbonate (MC) solvent and in PEO containing MC as a plasticizer. The MC was made by attaching three ethylene oxide units to the 4-position of ethylene carbonate. The potassium salt was di-potassium N,N'-Jeffamine dipropanesulfonate (JDPS) and was synthesized at BNL. Figure 1 shows NEXAFS spectra for the potassium salt in MC at various temperatures. Surprisingly, ion pairing increases with increasing temperature. Figure 2 shows that at 25°C the addition of MC to PEO increases ion dissociation.

Fig.1. Effect of temperature on K NEXAFS in a JDPS salt/MC solution; salt/MC weight ratio = 100/40.

Fig. 2. Effect of MC additions on K NEXAFS in a JDPS salt/PEO complex with MC as a plasticizer; the salt/PEO/MC weight ratios are (a) 100/80/40, (b) 100/100/40 and (c) 100/100/80.

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X-19C

CHARACTERIZATION OF GROWTH DEFECTS IN KTA SINGLE CRYSTALS †

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Single crystal potassium titanyl arsenate (KTA) is a nonlinear optical material with large nonlinear optical coefficient and high laser damage threshold. The defect structure of flux grown KTA single crystals has been studied by synchrotron white beam X-ray topography. Fig.1 ($g = 301$) is a topograph recorded from an (010) plate which was cut through the seed crystal (S). Defects such as dislocations (D), growth sector boundaries (G), inclusions (I), growth bands (B), are imaged. Cracks (C), and surface scratches (X) are also imaged. The major growth sectors are identified as $\{100\}$, $\{101\}$, and $\{011\}$. The most prominent defects are growth dislocations originating from the seed surfaces. The dislocations observed are straight and follow a number of discrete line directions being close to the normals of the growth sectors where they lie. The dislocations are located predominantly in the $\{100\}$ sectors and the dislocation density of other parts of the crystal is very low. The topograph also reveals the growth history of the crystal. Both growth bands and curved growth sector boundaries indicate fluctuations in growth conditions. It is notable that all of the dislocations are nucleated from the seed surface which indicates that the period of initial growth is not optimal. The fact that most of the dislocations lie in the $\{100\}$ growth sector, means that large-volume, dislocation free crystals can be grown by judicious selection of the shape of seed crystals.

Figure 1

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X-19C

INVESTIGATION OF GROWTH DEFECTS IN FLUX GROWN KTP SINGLE CRYSTALS BY SYNCHROTRON WHITE BEAM X-RAY TOPOGRAPHY †

H. Chung, S. Wang, and M. Dudley (SUNY Stony Brook), L. K. Cheng, J. D. Bierlein, and W. Bindloss (E. I. duPont, Wilmington, DE)

Potassium titanyl phosphate (KTP) has been shown to be an excellent nonlinear optical material. It has many attractive properties for optical and electro-optical applications such as high laser damage threshold, good mechanical and thermal stability, and large optical nonlinearity. KTP can be grown by both hydrothermal and flux methods, although large size crystals are best grown by the latter method. In this report, a KTP single crystal grown by the flux method is investigated by synchrotron white beam X-ray topography. Fig.1 is a topograph of a (210) KTP slice. Prominent growth sector boundaries (B) are indicated on the topograph. In addition growth defects such as dislocations (D) mainly lying on the $\{011\}$ sectors, inclusion (I), and surface scratches (S) are imaged. The slice intersects four growth sectors corresponding to the (210), (011), (011) and (100) sectors. The fringe contrast revealing the growth sector boundaries results from dynamical diffraction effects and indicates that the boundaries are faulted and have a very low level of lattice strain associated with them.

Figure 1

† Acknowledgements: Work performed on the Stony Brook Synchrotron Topography Facility, Beamline X-19C, and supported by E. I. duPont de Nemours & Company, Inc.

OBSERVATION OF INTERACTIONS BETWEEN DISLOCATIONS AND GROWTH SECTOR BOUNDARIES AND GROWTH BANDS IN KTA USING SYNCHROTRON WHITE BEAM X-RAY TOPOGRAPHY †

H. Chung, S. Wang, and M. Dudley (SUNY Stony Brook), L. K. Cheng and J. D. Bierlein, and W. Bindloss (E. I. duPont, Wilmington, DE)

Grown-in dislocations, in general, follow straight lines with preferred directions close to the growth direction. However, the deviation of dislocations from these straight paths can occur when the growth environment is changed. Deviation of dislocations from straight paths has been observed in KTA single crystals as shown in Fig.1 and Fig.2. Fig.1 shows the abrupt change of dislocation line direction at growth sector boundaries. Since the growth direction is changed, dislocations D_1 undergo a sharp bend as they penetrate the growth sector boundary (G). In Fig.2, the deviation of dislocation line direction by growth bands (B) is imaged. The long-range stress associated with the growth bands, gives rise to forces which produce a zig-zagging effect on the penetrating dislocations, D_2 .

Figure 1

Figure 2

† Acknowledgments: Work performed on the Stony Brook Synchrotron Topography Facility, Beamline X-19C, and supported by E. I. duPont de Nemours & Company, Inc.

OBSERVATION OF {011} FERROELECTRIC DOMAIN WALLS IN FLUX GROWN KTP SINGLE CRYSTALS BY SYNCHROTRON WHITE BEAM X-RAY TOPOGRAPHY †

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Potassium titanyl phosphate (KTP), an important nonlinear optical material, is ferroelectric with polar axis along the crystallographic b axis ($b=10.6\text{\AA}$). The presence of domains increases the electro-optic switching voltages and decreases the efficiency of nonlinear optical conversion. Techniques such as piezoelectric measurements, electrostatic toning, and X-ray anomalous dispersion have, in the past, been employed in detecting ferroelectric domains. We report here the use of synchrotron white beam x-ray topography for direct observation of {011} ferroelectric domain walls in flux grown KTP crystals. Fig. 1 is a topograph ($g = 010$) showing a zig-zagging ferroelectric domain wall (F) in a (100) KTP plate. Detailed analysis of the projected directions of the domain wall image segments on different reflections shows that the wall orientation oscillates between (011) and (01 $\bar{1}$). The fringe contrast revealing the domain wall results from interference between the original wavefields traveling in the crystal and phase shifted wavefields created upon crossing the boundary. The phase difference between the two kinds of wavefield is given by $\delta_{hkl} = 2\pi \mathbf{g} \cdot \mathbf{u} + \alpha_{hkl}$, where $\mathbf{g}$ is the diffraction vector, $\mathbf{u}$ is the fault vector associated with the boundary, and α_{hkl} is the difference in the phase angle of the structure factor for the domains. In Fig. 2 ($g = 011$) and Fig. 3 ($g = 01\bar{1}$), regions of the domain wall become almost invisible, due to extinction of the fringe contrast. This means that for these reflections $\delta_{hkl} = 0$. This analysis can be used to determine the fault vector, $\mathbf{u}$, of the wall. The residual contrast present on figures 2 and 3 is thought to result from long range strain associated with the wall. The fact that this contrast is strongest when the $\mathbf{g}$ vector is parallel to the wall plane indicates that the orientation of the displacement vector associated with the long range strain field also lies in the wall plane.

Figure 1 1mm

Figure 2 1mm

Figure 3

† Acknowledgments: Work performed on the Stony Brook Synchrotron Topography Facility, Beamline X-19C, and supported by E. I. duPont de Nemours & Company, Inc.

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USING SYNCHROTRON WHITE BEAM X-RAY TOPOGRAPHY TO CHARACTERIZE FERROELECTRIC DOMAIN WALLS IN KTP SINGLE CRYSTALS †

H. Chung, S. Wang, and M. Dudley (SUNY Stony Brook), L. K. Cheng, J. D. Bierlein, and W. Bindloss (E. I. duPont, Wilmington, DE)

Ferroelectric domain walls (F) in both hydrothermal and flux grown KTP single crystals have been studied by synchrotron white beam x-ray topography. Ferroelectric domain walls are revealed by the fringe contrast, F, shown in Fig. 1. The fringe contrast is attributed to interference effects associated with the phase shift experienced by the x-ray wavefields as they cross the domain walls. The phase shift due to ferroelectric domain boundaries or inversion twin boundaries is given by $\delta_{hkl} = 2\pi \mathbf{g} \cdot \mathbf{u} + \alpha_{hkl}$, where $\mathbf{g}$ is the diffraction vector, $\mathbf{u}$ is the fault vector associated with the boundary, and α_{hkl} is the difference in the phase angle of the structure factors for two adjacent domains. The fringe contrast will be invisible when $\delta_{hkl} = 2m\pi$, where m is either 0 or an integer. In order to characterize the ferroelectric domain walls, section topography can also be employed since dynamical effects are more pronounced than on corresponding integrated topographic images. The advantages of using synchrotron radiation are that section topography experiments can be conveniently carried out with exposure times of just a few minutes, and that very critical adjustments of the crystal orientation are not necessary. Fig. 2 shows a section topograph of ferroelectric domain walls. In this case the interference effects give rise to the well known "hour-glass" contrast which results from the phase shift when x-ray wavefields cross the boundary. Detailed analysis of the variation in contrast from the walls on different reflections confirms that the contrast arises from an inversion twin or ferroelectric domain scenario [1].

Figure 1

Figure 2

Reference 1. S. Wang, M. Dudley, L. K. Cheng and J. D. Bierlein, *Mat. Res. Soc. Symp. Proc.* 307, 243 (1993)

† Acknowledgments: Work performed on the Stony Brook Synchrotron Topography Facility, Beamline X-19C, and supported by E. I. duPont de Nemours & Company, Inc.

X-19C

SYNCHROTRON WHITE BEAM X-RAY TOPOGRAPHY STUDY OF DISLOCATION PROPAGATION FROM INCLUSIONS IN CdTe(111)B†

T. Fanning, M. Dudley (SUNY Stony Brook), and M.B. Lee (Grumman Corporate Research Center).

We have recently shown using white beam synchrotron topography, that the mechanism of contrast formation from inclusions in CdTe substrates involves significant local lattice rotation associated with the plastic deformation surrounding the inclusion.^{1,2,3} In addition to observing these highly plastically deformed regions, individual dislocations propagating out from the inclusions are also revealed using topographic imaging. Figure 1a is a detail from a 333 reflection ($\lambda=0.89\text{\AA}$) of a CdTe substrate showing the contrast arising from inclusions I and the groups of dislocations D propagating out from the inclusion in the (011). Figure 1b and 1c are similar images ($g=333$, $\lambda=0.89\text{\AA}$) recorded from an MBE grown CdTe:CdTe(111)B film. The low defect density of the CdTe epilayer allows clear resolution of individual dislocations propagating out from the inclusion in the (011). Thus the deleterious effects of inclusions on the structural quality of CdTe epitaxial films can be demonstrated.

Figure 1.

References: 1. T. Fanning, M.B. Lee, L.G. Casagrande, D. DiMarzio, and M. Dudley, "Synchrotron White Beam X-ray Topography Analysis of MBE Grown CdTe/CdTe(111)B", *Journal of Electronic Materials*, 22, 943, (1993); 2. T. Fanning, M. Dudley, M.B. Lee and L.G. Casagrande, "White Beam Synchrotron Transmission Topography of Inclusions in Ultrathin CdTe Single Crystals", *1992 National Synchrotron Light Source Annual Report*; 3. M.B. Lee, T. Fanning, D. DiMarzio, L.G. Casagrande, and M. Dudley, "Optimization of MBE Growth of CdTe/CdTe: Refinement in Structural Quality Evaluation of MBE Grown (111) CdTe", in "Defect Engineering in Semiconductor Growth, Processing and Device Technology", S. Ashok, J. Chevallier, K. Sumino, and E. Weber (Eds.), *Mat. Res. Soc. Symp. Proc.*, 262, 215-220, (1992).

† Acknowledgements: Work performed on the Synchrotron Topography Project Beamline X-19C, and supported by Grumman Corporate Research Center

X-19C CHARACTERIZATION OF SUPER-SCREW DISLOCATIONS IN 6H-SiC DEVICES †

W. Huang, S. Wang, M. Dudley (SUNY Stony Brook), C. Fazi (U.S. Army Research Laboratory, Adelphi, MD)

6H-SiC has attracted widespread interest due to its excellent physical and electronic properties such as its wide bandgap, high electric breakdown field, high thermal conductivity and high saturated electron drift velocity. The quality of the 6H-SiC single crystals, especially in epitaxial layers, is very important for device fabrication. Epitaxial layers of 6H-SiC can be obtained by liquid-phase epitaxy (LPE) or vapor-phase epitaxy (VPE) at high temperature on 6H-SiC substrates, which are commercially available in one inch wafers. Growth of Epitaxial SiC by CVD seems to be the currently preferred technique. The orientation and the quality of the 6H-SiC substrates, as well as the epitaxial growth temperature, determine the quality of the epitaxial layer. Defects in the epitaxial layers can be detected using Synchrotron White Beam X-ray Topography. Super-screw dislocations were imaged inside devices on a 250 μ m thick, 6H-SiC (0001) wafer, as shown in Fig. 1. The size of the Burgers vector and the distribution of these dislocations varies between individual devices. The dislocation density is very high in some devices, while it is relatively low in others. We have recently shown¹ that super-screw dislocations in SiC tend to form into groups with a resultant Burgers vector which can be many times the magnitude of that of an individual dislocation, giving rise to very broad images such as those indicated at S on Fig. 1. Both high densities of relatively small Burgers vector dislocations and lower densities of very large Burgers vector dislocations are undoubtedly harmful to device performance.

Figure 1

Reference

- [1] S. Wang, M. Dudley, C. Carter, Jr., D. Asbury and C. Fazi, *Mat. Res. Soc. Symp. Proc.*, **307**, 249 (1993)

† Acknowledgements: Work performed on the Synchrotron Topography Project Beamline X-19C, and supported by U.S. Army Research Laboratory

X-19C OBSERVATION OF DEFECTS IN SiC DEVICES BY SYNCHROTRON WHITE BEAM X-RAY TOPOGRAPHY †

W. Huang, S. Wang, M. Dudley (SUNY Stony Brook), C. Fazi (U.S. Army Research Laboratory, Adelphi, MD)

6H-SiC has great potential for high-power, high-frequency operation because of its excellent physical and electronic properties.¹ It is capable of implementation in devices designed for many applications. One such application is the impact ionization avalanche transit time (IMPATT) diode, as shown in Fig. 1, which is a Nomarski micrograph showing such a device on a 250 μ m thick 6H-SiC, (0001) wafer. Synchrotron White Beam X-ray Topography has been used to study the location and character of defects in relation to the device. Since the quality of the near surface region is the most important in device operation, the surface sensitive grazing reflection geometry was used so that the x-ray penetration depth would be small enough to study the defects just a few microns beneath the sample surface, i.e., in the epitaxial region. Fig. 2 is a reflection topograph recorded from the same region of crystal ($g = 1109$, $\lambda = 0.76$ Å). The white elliptical features inside the device, marked S, are super-screw dislocations. These dislocations exist in the substrates and are replicated during epitaxial growth, so they are parallel to the growth direction, i.e., perpendicular to the basal plane. The Burgers vector of these super-screw dislocations can be very large,² leading to the existence of their hollow cores.³ Such defects will undoubtedly influence the operation of the device, for example preventing the diode from producing the proper negative resistance to keep the current lagging behind the voltage. Correlation between the presence of these super-screw dislocations, i.e., their detailed position with respect to the device topology, and device performance, is the subject of an ongoing investigation.

Figure 1

Figure 2

References

- [1] J. W. Palmour, J. A. Edmond, H. S. Kong, C. H. Carter Jr., *J. Physica B*, **185**, 461 (1993).
- [2] S. Wang, M. Dudley, C. Carter, Jr., D. Asbury and C. Fazi, *Mat. Res. Soc. Symp. Proc.*, **307**, 249 (1993)
- [3] F. C. Frank, *Acta cryst.*, **4**, 497 (1957).

† Acknowledgements: Work performed on the Synchrotron Topography Project Beamline X-19C, and supported by U.S. Army Research Laboratory

X-19C **INVESTIGATION OF BREAKDOWN DAMAGE IN GaAs DEVICES BY SYNCHROTRON WHITE BEAM X-RAY TOPOGRAPHY †**

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Improvements in GaAs material and wafer fabrication processes have resulted in an assortment of low-noise chips, multiwatt amplifiers, and dense digital logic arrays for military and commercial use. Investigation of breakdown phenomena in many of these devices is of key importance to their implementation. Synchrotron White Beam X-ray Topography is a powerful tool for detecting structural damage induced by electromagnetic breakdown in devices.^{1,2} Fig. 1 shows a topograph, recorded in grazing incidence, from a device on a 150 μ m thick, 2x3mm² GaAs (100) crystal ($g = 313$, $\lambda = 1.00$ Å). The light area corresponds to that part of the image originating in the region of crystal beneath the metallization. This contrast arises mainly from absorption, due to the long effective path length inside the metallization. The upper right corner of the extinction contrast is also visible from the edge regions of the metallization. The upper right corner of the device (marked by an arrow), as shown in the Nomarski micrograph in Fig. 2 (a), has been electronically tested and was found to be damaged. Topographs recorded from this area were deliberately overexposed in an attempt to reveal evidence for damage. Fig. 2 (b) is the reflection topograph of this area ($g = 511$, $\lambda = 0.80$ Å). Close examination of the extinction contrast from some of the finer details of the metallization region apparently reveals damage which is not visible via optical microscopy. The implications of these observations on the understanding of the failure mechanism are currently under investigation.

Figure 1

Figure 2

References

- [1] M. Dudley, G. Tolis, D. Gordon-Smith and C. Fazi, *Materials Science and Engineering*, **B15**, 56 (1992)
- [2] S. Wang, M. Dudley, C. Fazi, D. Gordon-Smith, *Mat. Res. Soc. Symp. Proc.*, **307**, 237 (1993)

† Acknowledgements: Work performed on the Synchrotron Topography Project Beamline X-19C, and supported by U.S. Army Research Laboratory

X-19C **DETAILED OBSERVATION OF THE MECHANISMS INVOLVED IN TEMPERATURE-CHANGE INDUCED MICROSTRUCTURAL CHANGES IN POLYCRYSTALLINE ICE.†**

F. Liu, I. Baker (Dartmouth College), and M. Dudley (SUNY Stony Brook).

Detailed observations have been made of the formation and disappearance of individual unfaulted dislocation loops, individual faulted dislocation loops, and concentric dislocation loops connected by stacking faults, all created by interstitial condensation on the basal plane. The mechanisms involved are similar to those proposed for hexagonal metals, due to the similarities between the structures.^{1,2} Initially, upon cooling, a single layer disk of interstitials is formed between adjacent basal planes, i.e. a faulted dislocation loop with $b=R=1/2[0001]$ (where b is the Burgers vector, and R is the fault vector). This can then be converted to a double-layer unfaulted loop, with $b=[0001]$, via a mechanism involving the single layer loop being consecutively swept by two partial dislocations. As pointed out by Amelinckx,² it is energetically favorable for the $[0001]$ unfaulted dislocation loop to dissociate into two partial dislocations on adjacent basal planes, which can climb conservatively to yield the kind of concentric dislocation loops connected by stacking faults observed upon cooling. This latter sequence of configurations is shown schematically in figure 1(a)-(c). Figure 2(a)-(c) shows a detailed view of the evolution of the stacking fault configuration achieved by slow annealing.

Figure 1.

Figure 2.

References: 1. T. Hondoh and A. Higashi, *J. Phys. Chem.*, **87**, 4040, (1983); 2. S. Amelinckx in "Dislocations in Solids, Vol. 2, F.R.N. Nabarro (ed.), North-Holland, Amsterdam, 1979, Chapter 6, p. 313.

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DISLOCATION ANALYSIS IN ICE†

F. Liu, I. Baker (Dartmouth College), and M. Dudley (SUNY Stony Brook)

Figure 1(a) ($g=1010$), (b) ($g=0110$) and (c) ($g=1100$) show a typical dislocation structure inside a large grain in an ice polycrystal. Figure 1(d) is a schematic of the dislocation structure. Table I shows the result of detailed Burgers vector and line direction analysis. In this table, "V" stands for visible, while "I" stands for invisible. Screw, 30° and 60° dislocations with Burgers vectors of $\langle 1120 \rangle$ type, lying on basal planes, outnumber other kinds of dislocations.¹

Figure 1.

dislocation number	a (1010)	b (0110)	c (1100)	d	line direction
1	V	I		(2110)	60°
2	V		I	(1120)	screw
3	V	I		(2110)	30° screw
4	I		V	(1210)	30°
5	I		V	(1210)	screw
6	V	I		(2110)	30° screw
7	V	I		(2110)	30° screw
8	I		V	(1210)	screw
9	V	I		(2110)	mixed
10	V	I	I	(1120)	screw
11	V	I		(2110)	60° screw, 60°
12	I	V		(1210)	screw
13	V		I	(1120)	30°
14	V		I	(1120)	30°
15	I	V		(1210)	30° screw
16	I	V		(1210)	screw

Table I

References: 1. T. F. Liu, PhD Thesis, Dartmouth College, (1992).

† Acknowledgements: Research supported by the U.S. Army Research Office through grants numbers DAAL03-92-G-0319 and DAAH04-93-G-006 and in part by the donors of the Petroleum Research Fund which is administered by the American Chemical Society. Professor E.M. Schulson is acknowledged for the use of the Ice Research Laboratory.

DISLOCATION RECOVERY IN ICE CRYSTALS†

F. Liu, I. Baker (Dartmouth College), and M. Dudley (SUNY Stony Brook).

Observation of stress-induced dislocation dynamics in ice using X-ray topography carried out with conventional sources is complicated by dislocation recovery (thermally activated dislocation motion after the stress is removed). This problem was investigated using synchrotron white beam topography. A sample containing three columnar grains was subjected to a compressive stress at -14.5°C . Figure 1(a) shows the dislocation structure in one of the grains (which were initially dislocation-free) immediately after the stress was removed. Note the numerous semi-hexagonal loops generated from sources at the grain boundary, which is located at the upper part of the image. Figure 1(b) shows a different reflection, recorded from the same grain, ten minutes after figure 1(a). Note the rounding of the corners of the semi-hexagonal loops, and the small degree of dislocation motion. Evidently, significant recovery occurs over the time scale it takes to record an X-ray topograph using conventional radiation, which is at best ten minutes. Therefore, conventional X-ray topography cannot reveal the true dynamic behavior of dislocations in ice, underlining the importance of carrying out such studies using synchrotron white beam topography.¹

Figure 1.

References: 1. T. F. Liu, I. Baker, and M. Dudley, Phil. Mag. A, 67, 1261, (1993).

† Acknowledgements: Research supported by the U.S. Army Research Office through grants numbers DAAL03-92-G-0319 and DAAH04-93-G-006 and in part by the donors of the Petroleum Research Fund which is administered by the American Chemical Society. Professor E.M. Schulson is acknowledged for the use of the Ice Research Laboratory.

X-19C FORMATION OF FAULTED PRISMATIC DISLOCATIONS VIA INTERSTITIAL CONDENSATION IN ICE†

F. Liu, I. Baker (Dartmouth College), and M. Dudley (SUNY Stony Brook).

It is well known that stacking faults in ice can be produced through condensation of interstitials induced by cooling.¹ Although such faults produced by slow and moderate cooling have been studied extensively, no detailed studies of stacking faults formed by rapid cooling have been reported, presumably because of the high speed at which the microstructure changes. Figure 1 shows a configuration of stacking faults produced in a one half of a bicrystal of ice in which the basal planes made an angle of 30° to the large surface of the specimen. The acuteness of this latter angle of intersection makes it difficult for the interstitials, which exist in the lattice at the starting temperature (-20°C), to diffuse on the basal planes and out of the crystal, so that they get trapped and "condense" when the crystal is rapidly cooled to -60°C. The observed configurations of individual unfaulted dislocation loops, individual faulted dislocation loops and concentric dislocation loops connected by stacking faults are evidence for the processes of interstitial segregation and condensation on the basal plane which are similar to those proposed for hexagonal metals.^{2,3}

Figure 1.

References: 1. T. Hondoh and A. Higashi, Japan. J. Appl. Phys., 20, L737, (1981); 2. T. Hondoh and A. Higashi, J. Phys. Chem., 87, 4040, (1983); 3. S. Amelinckx in "Dislocations in Solids, Vol. 2, F.R.N. Nabarro (ed.), North-Holland, Amsterdam, 1979, Chapter 6, p. 313.

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X-19C INVESTIGATION OF THE ORIENTATION DEPENDENCE OF STACKING FAULT DEPLETED ZONES NEAR GRAIN BOUNDARIES IN ICE†

F. Liu, I. Baker (Dartmouth College), and M. Dudley (SUNY Stony Brook).

In order to study the effect of the orientation of the basal planes with respect to a grain boundary or free surface on the size of the stacking fault depleted zone, an ice bicrystal was made which had a large-angle grain boundary parallel to the largest surfaces. Each grain had a thickness of 1mm. The basal plane for grain 1 made an angle of about 30° with the boundary, while that for grain 2 was nearly perpendicular to the boundary. The crystal was then cooled from -20°C to -60°C over a period of about thirty minutes. Following this, the crystal was slowly warmed back up to -20°C over a period of two hours. In grain 1, the initial rapid cooling produced various configurations of both faulted and unfaulted dislocations loops - all evidence for interstitial condensation (see figure 1(a) and (b)), whereas in grain 2, no such condensation occurred (see figure 2(a) and (b)). This suggests that the size of the depleted zone near a grain boundary is a function of the angle between the basal plane and the boundary, and implies that diffusion in ice occurs mainly on the basal plane. These observations are consistent with the larger measured values of water molecule diffusion coefficient perpendicular to the c-axis compared to those measured parallel.¹⁻³ During annealing, some concentric loops disappeared (e.g. at A, B and C in 1(a)), while others transformed into perfect prismatic loops (e.g. at D, E and F).

Figure 1.

Figure 2.

References: 1. P.V. Hobbs, "Ice Physics", Clarendon Press, Oxford, (1974), p. 382; 2. R.O. Ramseier, J. Appl. Phys., 38, 3553, (1967); 3. K. Itagaki, J. Phys. Soc. Japan, 22, 427, (1967).

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ORIENTATION DEPENDENCE OF SLIP IN ICE POLYCRYSTALS†

F. Liu, I. Baker (Dartmouth College), and M. Dudley (SUNY Stony Brook).

Since basal slip is the most important deformation mechanism in polycrystalline ice, it is of interest to examine the situation where the Schmid Factor for basal slip is near zero. To this end, an ice bicrystal, with the grain boundary perpendicular to the stress axis, was deformed in compression. One of the grains had its basal planes also almost perpendicular to the stress axis. Under these conditions, neither grain boundary sliding nor basal slip are favored. Despite prolonged application of significant stresses, only elastic strain fields were produced at the boundary (located at the upper part of the image), as shown in figure 1. A very small degree of motion of a single dislocation, marked **L** was noted. This was due to a small residual resolved shear stress on the basal planes, due to the fact that these planes were not exactly perpendicular to the stress axis. Some of the pre-existing dislocations slipped out at the free surface, but no lattice dislocations were generated from the grain boundary, despite the large internal stress fields indicated by the dark contrast.¹

(a)

(b)

Figure 1.

References: 1. T. F. Liu, I. Baker, and M. Dudley, Phil. Mag. A, 67, 1261, (1993).

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OBSERVATION OF BONDING STRAIN IN SC CUT QUARTZ RESONATORS.†

W. Si and M. Dudley (SUNY Stony Brook); T. McClelland, M. Bloch, R. Regis, B. Goldfrank and S. Seifer (Frequency Electronics, Inc. Mitchel Field, NY).

Two aspects of the frequency stability of crystal resonators are of practical interest, long-term stability or aging and short-term stability. The chief mechanism for the former includes stress effects, mass loading effects, and materials effects. In this study, the strain due to the bonding process has been investigated. The resonators are 5 MHz, fifth overtone, SC cut precision resonators with three nickel-ribbon pins attached to the quartz crystal blanks by thermal-compression (TC) bonding. Figures 1 and 2 show the reflection topographs of resonator No.1 and No.2 ($g = 220, \lambda = 0.76 \text{ \AA}$). The dislocations (D) intersecting the surface are visible on both images. However, strain (S) due to TC bonding in three pin positions is evident in figure 1 but not in figure 2. The fact that TC bonding introduces strain around pin positions in some resonators, while not in others, is indicative of an inconsistency in the manufacturing process.

Figure 1

Figure 2

† Acknowledgments: Work performed on the Synchrotron Topography Project Beamline X19C, and supported by the Frequency Electronics, Inc.

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OBSERVATION OF ELECTRODE STRAIN IN SC CUT QUARTZ RESONATORS.†

W. Si and M. Dudley (SUNY Stony Brook); T. McClelland, M. Bloch, R. Regis, B. Goldfrank and S. Seifer (Frequency Electronics, Inc. Mitchel Field, NY).

Gold thin film electrodes deposited on the quartz resonator blank surfaces at high temperature can create stress, which can potentially affect the frequency stability of resonators. In this study, X-ray transmission topography was carried out to analyze the stress environment of the electrode-blank interface. The metal-film electrodes, with thickness of several hundred Å, are on both sides of the blank. Figure 1 shows a transmission topograph of an SC cut 5MHz resonator ($g = \bar{1}01, \lambda = 0.66 \text{ Å}$). The strain at the edge of the electrode is indicated by S. D indicates dislocation. The sign and direction of strain have been determined by $g \cdot u = 0$ analysis, where u is the displacement vector. The results show that u is normal to the film edge, so that there is no shear stress. From the different contrast (black or white) at the different segments of electrode edge, it can be inferred that the stress in the blank is in compression, which coincides with the difference in thermal expansion coefficient between quartz and gold.

Figure 1

† Acknowledgments: Work performed on the Synchrotron Topography Project Beamline X19C, and supported by the Frequency Electronics, Inc.

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PENDELLÖSUNG FRINGES IN TRANSMISSION X-RAY TOPOGRAPHS OF SC CUT QUARTZ RESONATORS.†

W. Si and M. Dudley (SUNY Stony Brook); T. McClelland, M. Bloch, R. Regis, B. Goldfrank and S. Seifer (Frequency Electronics, Inc. Mitchel Field, NY).

Contouring uniformity in SC cut 5MHz 5th overtone quartz resonators has been investigated using transmission X-ray topography. The crystal surfaces are both convex, so that equi-thickness type Pendellösung fringes can be observed on transmission topographs. The local thickness of convex-convex wafer is determined by the maximum thickness at the center and the curvature of the surface. Elliptical Pendellösung fringes are observed to cover the whole resonator surface, as shown in Figure 1 ($g = 01\bar{1}, \lambda = 0.54 \text{ Å}$). The X-ray extinction distance for this reflection is $91 \mu\text{m}$. The maximum variation in wafer thickness is about $250 \mu\text{m}$ so that, when projection effects are taken into account, three to four fringes are expected. The shape and uniformity of these fringes can be used as a non-destructive gage of the quality of the surface contouring. In addition, the fringe spacing is seen to decrease in the vicinity of the three pin positions, as indicated by P on the figure. This is due to the strain associated with the thermal-compression bonding process used to attach the pins.

Figure 1

† Acknowledgments: Work performed on the Synchrotron Topography Project Beamline X19C, and supported by the Frequency Electronics, Inc.

X-19C **X-RAY REFLECTION TOPOGRAPHY STUDIES OF QUARTZ CRYSTAL BARS.[†]**

W. Si and M. Dudley (SUNY Stony Brook); T. McClelland, M. Bloch, R. Regis, B. Goldfrank and S. Seifer (Frequency Electronics, Inc. Mitchel Field, NY).

α -quartz is the materials basis of a significant portion of the frequency control and communication industry. It is believed that defects in the crystals can cause problems in resonator performance, such as accelerated sensitivity, thermal hysteresis and possibly aging. X-ray reflection topography has been used to study defects in synthetic quartz crystal bars of premium Q which are used to make high precision SC cut quartz resonators. The quartz bars, grown by the hydrothermal method, are of X and Z surface orientations. Bar dimensions are about 17cm $\times$ 1.6cm $\times$ 1.5cm. The bars have been subjected to the sweeping process which is an electric-field driven, solid-state diffusion process at an elevated temperature. Figure 1 shows reflection topographs of such a quartz crystal bar, where for the +X surface, $g = 3\bar{1}21, \lambda = 0.86 \text{ \AA}$; for the -X surface, $g = 3211, \lambda = 0.81 \text{ \AA}$; for the +Z surface, $g = 1105, \lambda = 0.61 \text{ \AA}$; and for the -Z surface, $g = 1014, \lambda = 0.85 \text{ \AA}$. In the $\pm X$ surfaces, surface scratches are visible. In the -Z surface topograph, the emergent ends of dislocations which may be decorated with impurities, constituting a subgrain structure, are observed. In the +Z surface topograph, precipitates are visible. These precipitates are probably produced by the sweeping process, which consists of applying electrodes to the Z surfaces of the bar and an electric field along the Z direction. Under the influence of high temperature and high electric field, impurity ions diffuse to the electrodes giving rise to surface precipitation.

Figure 1

1cm

[†] Acknowledgments: Work performed on the Synchrotron Topography Project Beamline X19C, and supported by the Frequency Electronics, Inc.

X-19C **X-RAY TOPOGRAPHIC STUDIES OF SINGLE ORGANIC HOURGLASS INCLUSION K₂SO₄ CRYSTALS[†]**

W. M. Vetter, M. Dudley (SUNY Stony Brook), B. Kahr (Purdue University)

Organic hourglass inclusions are crystals of simple ionic salts containing organic dyes included in, and coloring the crystals only in, specific growth sectors, sometimes in patterns resembling a hourglass or bow-tie shape. The complete discrimination of symmetry distinct inorganic surfaces of single crystals by organic dyes represents exquisite molecular recognition in the crystal growth process. Oriented aromatic molecules containing chromophores trapped in ordered ionic matrices are promising candidates for use in nonlinear optical devices or as solid state laser dyes. We have studied single crystals of K₂SO₄ grown from aqueous solutions containing millimolar concentrations of the dye acid fuchsin. The red dye is deposited only on the {110} faces of the crystals during their growth, resulting in a rose-colored hourglass outline of these faces' growth sectors inside otherwise colorless, oblong crystals. Topographs of two separate crystals are shown in figure 1. Pendellosung fringes are visible, indicating these crystals are of good quality. The {110} growth sectors, marked S, containing dye possess a higher degree of strain compared to the colorless regions of the crystal and therefore are visible by X-ray topography through their darker contrast. Farther from the point of crystal growth nucleation, this contrast, and therefore, the strain associated with these growth sectors, decrease. Dislocations, marked D, when encountering the dyed growth sector boundaries, can be seen to abruptly change direction to follow the boundary plane. There are also some rather large particulate inclusions, marked I, visible. The influence of different dye concentrations on crystal quality is still under investigation.

Figure 1

—g

1mm

[†] Acknowledgments: Work performed on the Synchrotron Topography Project Beamline X-19C, and funded in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

X-19C

DISLOCATION GENERATION ASSOCIATED WITH SURFACE RELAXATION IN PVT 6H-SiC SINGLE CRYSTALS. †

S. Wang, M. Dudley (SUNY Stony Brook) and C. Carter, Jr. (Cree Research, Inc., Durham, NC)

Dislocation structures in commercial PVT 6H-SiC single crystal wafers of (0001) orientation have been studied extensively using Synchrotron White Beam X-Ray Diffraction Topography [1]. Figure 1 is an example of X-ray transmission topographs, where there are two different types of dislocations: open-core super screw dislocations (S) with Burgers vectors which are a multiple of lattice constant c (15 Å in 6H SiC) and basal plane dislocations (D) with Burgers vectors around 3Å. The super screw dislocations are obviously growth dislocations since they follow the growth direction (approximately (0001)). The basal plane dislocations, on the other hand, are usually believed to have been generated during the post-growth cooling process via plastic deformation under mechanical and/or thermal stresses at high temperatures. However, a possible mechanism involving the surface relaxation or image force associated with the special case of super screw dislocation in 6H-SiC single crystals may also be operative, so that at least some of the basal plane dislocations are also very closely related to the crystal growth process. During crystal growth at temperatures above 2000°C, at which plastic deformation is readily achieved, the super screw dislocations running along the growth direction always intersect the growth front, a free surface. The image force due to the existence of the free surface, then, can provide a significant shear stress along the basal plane because of the large magnitude of the the Burgers vectors of the super screw dislocations (at least five times of that of the basal dislocations). This shear stress may in turn generate glide dislocations with much smaller Burgers vectors on the basal plane via the Frank-Read mechanism. A simple model is developed based upon Eshelby and Stroh's solution of a screw dislocation in a semi-infinite crystal [2], in which the shear stress component due to surface relaxation in the near surface region where a dislocation intersects the free surface can be estimated as: $\sigma_{rs} = \mu B / 2\pi r$, where μ is the shear modulus, B is the Burgers vector of a super screw dislocation and r is the radial distance from the axis of a screw dislocation, which can be taken as the radius of the open core of the super screw dislocations in the present case. On the other hand, the critical shear stress for creating a dislocation in the basal plane via Frank-Read mechanism is given as: $\sigma = \alpha \mu b / r$, where α is 0.65 for an edge dislocation and 0.5 for a screw dislocation, b is the Burgers vector and r is also taken as the radius of the open core of super screw dislocations. Since B is at least 5 times of b , it can be seen that the image force is large enough to create basal plane dislocations. An extensive quantitative calculation by taking into account the relaxation due to the surfaces of the open cores is still underway and a similar result is expected.

Figure 1

Reference: 1. S. Wang, M. Dudley, C. Carter, Jr., D. Asbury and C. Fazi, *Mat. Res. Soc. Symp. Proc.*, **307**, 249 (1993). 2. J.D. Ashelby and A.N. Stroh, *Phil. Mag.*, **42**, 1401 (1951).

† Acknowledgements: Work performed at the Stony Brook Synchrotron Topography Facility, Beamline X-19C, and supported by NIST and by Cree Research, Inc. (Durham, NC)

X-19C

ORIENTATION CONTRAST OF OPEN CORE SCREW DISLOCATIONS REVEALED BY SYNCHROTRON WHITE BEAM X-RAY RAY-TRACING TOPOGRAPHS. †

S. Wang, M. Dudley (SUNY Stony Brook), C. Carter, Jr. (Cree Research, Inc., Durham, NC)

Dislocation structures in commercial (0001) 6H-SiC single crystal wafers have been studied using Synchrotron White Beam X-ray Topography. Two different types of dislocations are imaged on the X-ray transmission topographs: super screw dislocations with giant Burgers vectors of at least 15 Å (the crystal lattice c parameter), and basal plane dislocations some of which, if not all, are believed to be generated by the image force associated with the super screw dislocations [1]. The small source size (0.35mm×0.15mm) coupled with the long source-specimen distance (25m) has greatly enhanced the angular resolution while maintaining no spatial resolution loss at specimen-detector distances up to about 20cm. Such unique capability has been utilized extensively in the current investigation of the unique dislocation structures in (0001) 6H-SiC single crystal wafers. In particular, X-ray ray-tracing topography, i.e. recording X-ray topographs under exactly the same diffraction conditions but at several different specimen-detector distances (D_{sd}), so that slight orientation changes in the vicinity of the super screw dislocation cores can be detected. From the ray-tracing topographs shown in Figure 1(a) and (b), which were recorded in two different D_{sd} , the super dislocation double images (D) exhibit shifts not only in the incident plane (parallel to g vector and perpendicular to the page), but also in the plane perpendicular to the incident plane, which indicates the enormous lattice rotations near the super screw dislocation cores. Since the super dislocations are approximately parallel with one another, opposite directions of shift in the incident plane correspond to two different signs of Burgers vectors. A more extensive quantitative analysis is still underway.

Figure 1

Reference: 1. S. Wang, M. Dudley, C. Carter, Jr., D. Asbury and C. Fazi, *Mat. Res. Soc. Symp. Proc.*, **307**, 249 (1993).

† Acknowledgements: Work performed at the Stony Brook Synchrotron Topography Facility, Beamline X-19C, and supported by NIST and by Cree Research, Inc. (Durham, NC)

SCANNING MECHANISM FOR SYNCHROTRON WHITE BEAM X-RAY TOPOGRAPHY. †

S. Wang, M. Dudley (SUNY at Stony Brook), and C. Carter, Jr., (Cree Research, Inc., Durham, NC)

Synchrotron White Beam X-ray Diffraction Topography is an efficient technique for characterizing structural defects in large single crystals. The exposure time for recording a synchrotron X-ray topograph is only a matter of a few seconds due to the high intensity of synchrotron radiation source, in contrast with exposure times of at least a few hours using conventional generators. However, the area of the synchrotron white X-ray beam at the goniometer is about 5cm in the horizontal direction but only about 5mm in the vertical direction. In addition, the intensity distribution is not uniform in the vertical direction. For large crystal wafers (one inch in diameter or larger), it takes many exposures to cover the whole wafer. Image overlap may even preclude the use of the full beam size. Figure 1(a) is an example of a composite topograph recorded from a one inch crystal wafer, made up of about 30 individual topographs. Composing such topographs of large crystals is very time-consuming. Therefore, a scanning mechanism has been developed, utilizing the fact that the horizontal beam size is large enough, so that a diffraction topograph can be recorded from the entire crystal wafer by scanning the crystal and the recorder simultaneously in the vertical direction, while the incident beam and all the other reflections are prevented from reaching the recording plane by a set of slits. Figure 1(b) is such a scanned topograph recorded from the same crystal wafer as in Figure 1(a), where the image inhomogeneity found in Figure 1(a) due to the uneven source intensity is completely eliminated. Such a scanning mechanism dramatically increases the speed of topographic experiments (by a factor of 20), which is especially suitable for screening of defects in large crystal wafers in large quantity. Since the scanned topographs contain the defect structure of the whole wafer, it is much easier to analyse such defects in specific areas of interest.

Figure 1

† Acknowledgements: Work performed at the Stony Brook Synchrotron Topography Facility, Beamline X-19C, and supported by NIST and by Cree Research, Inc. (Durham, NC)

STUDY OF DEFECTS IN 6H-SiC EPITAXIAL THIN FILMS ON PVT 6H-SiC SUBSTRATES. †

S. Wang, M. Dudley (SUNY at Stony Brook), C. Carter, Jr., (Cree Research, Inc., Durham, NC)

SiC has been studied extensively recently, not only because of its superior physical and electronic properties, but also because of the availability of large single crystal wafers of crystalline perfection adequate for device fabrication. Similar to the device fabrication procedures in other semiconductors, e.g. Si and GaAs, the deposition of epitaxial thin films is essential. The growth temperatures for epitaxial thin films are usually significantly lower than that for the bulk crystal growth and the impurity concentrations of the source materials for epitaxial growth can be dramatically reduced, both of which contribute to better controlled electronic properties of the resultant epitaxial thin films. We report here the evidence that, apart from forementioned benefits of epitaxial growth, the defect density in the epilayers can also be lowered, as revealed by Synchrotron White Beam X-Ray Topography. The PVT 6H-SiC (0001) substrates (off-cut by a few degrees) and the subsequently grown 6H-SiC thin films (about 6 μ m thick) were examined by using surface-sensitive grazing incidence Bragg-Laue reflection technique. The reflection topograph shown in Figure 1(a) is from part of a substrate before epitaxial growth, where the super screw dislocations (the faint lines between super dislocations as indicated by B) are imaged. Figure 1(b) is a topograph recorded from the epilayer grown on the same region of the wafer under exactly the same diffraction conditions (particularly the same X-ray penetration depth, 5 μ m), where the super screw dislocations in the substrate are exactly replicated in the epilayer while the basal plane dislocations are not. Such a result may be explained by the fact that the epilayers were grown at relatively low temperatures (several hundred degrees lower than for the PVT bulk growth) at which plastic deformation via dislocation generation is so difficult that no basal plane dislocations could be generated during growth by the image force associated with super screw dislocations, a dislocation generation mechanism suggested for the case of PVT growth of bulk SiC crystals [1].

Figure 1

Reference: 1. S. Wang, M. Dudley, C. Carter, Jr., D. Asbury and C. Fazi, *Mat. Res. Soc. Symp. Proc.*, 307, 249 (1993).

† Acknowledgements: Work performed on the Synchrotron Topography Project Beamline X-19C, supported by NIST through Advanced Materials Program and by Cree Research, Inc. (Durham, NC)

X-19C

STUDY OF POLYTYPES IN COMMERCIAL PVT 6H-SiC SINGLE CRYSTAL USING SYNCHROTRON WHITE BEAM TOPOGRAPHY. †

S. Wang, M. Dudley (SUNY Stony Brook), C. Carter, Jr. (Cree Research, Inc., Durham, NC)

SiC exhibits one of the classic examples of polytypism whereby the tetrahedrally coordinated Si-C double layers crystallize into many different stacking sequences. The common polytypes are 6H, 15R, 4H and 3C. Even these common polytypes have different electronic properties, for example band-gap and carrier mobility, which will result in different device characteristics. Therefore, single crystals of a single polytype, particularly 6H, which is very important in applications such as blue LEDs, are necessary for device fabrication. Currently, the seeded Physical Vapor Transport method has been very successful in growing large size (over one inch in diameter) 6H SiC single crystal boules. However, such boules often have large areas of 6H center regions surrounded by polycrystals and polytypes, and so the wafers cut from such boules may contain some polytypes, usually 15R, on the edges. Synchrotron White Beam X-ray Topography is particularly suitable for studying such polytypes. Figure 1(a) is an example of a laue transmission pattern from the edge of a one-inch 6H SiC wafer, where the polytype is determined to be 15R. By examining the individual topographs, as shown in Figure 1(b), the 15R polytype region is found to be embedded in the 6H matrix with curved inter-polytype boundaries. The dislocations, i.e. the super screw dislocations (S) and the basal plane dislocations (the net-work structures) in the 6H matrix region beneath the 15R polytype are clearly resolved. On the topograph from the 15R polytype, however, only the super screw dislocations were imaged, possibly due to the fact that the contrast associated with the strain in the 15R polytype region overwhelms the contrast from basal plane dislocations. The polytype crystal region can be observed readily under optical microscope in transmission mode where the contrast can be attributed to the strain-induced refractive index changes at the inter-polytype boundaries. The mechanism of polytype formation is still under investigation.

Figure 1

† Acknowledgements: Work performed on the Synchrotron Topography Project Beamline X-19C, and supported by NIST and by Cree Research, Inc. (Durham, NC)

X-19C

ANALYSIS OF DEFECT STRUCTURES IN LELY 6H-SiC SINGLE CRYSTAL PLATES. †

S. Wang, M. Dudley (SUNY Stony Brook), C. Fazi (Army Research Laboratory, Adelphi, MD)

SiC single-polytype crystal plates of several millimeters in diameter were grown by the Lely method as early as 1960. Although the Lely method does not seem to readily adapt to the production of large single crystal wafers, selected Lely crystal plates are still the best in terms of crystalline perfection and they are, as recently, used as seed crystals in PVT crystal growth, which is a commercially viable process for producing SiC wafers. On the other hand, because of the high perfection of the Lely plates, special semiconductor devices of small quantity may also be fabricated on these Lely crystal plates, which may exhibit a better performance than on the commercial PVT crystal wafers. High quality 6H-SiC Lely crystal plates, about 8mm across and 0.5 mm thick, have been examined by Synchrotron White Beam X-Ray Topography. Figure 1(a) is an example of X-ray transmission topographs recorded from such a plate. The crystal plate had contact with the graphite crucible (indicated by arrowheads) where the nucleation started. Most dislocations imaged on the topograph are growth dislocations with Burgers vectors in the basal plane (D), since they follow the growth fronts which are the prismatic planes. There are no super screw dislocations with giant Burgers vectors along the crystallographic c axis observed in these plates, in contrast with routine observations of high densities of such super dislocations (10^4 – 10^5 cm⁻²) in PVT 6H-SiC wafers. There is also a void (V) or a group of voids in the middle of the plate, since this region is shown to be less absorbing on the X-ray radiographs recorded. This is probably due to a so-called growth accident, and dislocations also nucleate from this region, some of which are glide dislocations (looping around the void) generated under the stress in the void region during post-growth cooling. Obviously, the crystal tends to grow much faster in the directions in the basal plane than in the basal plane normal direction, so that the crystal has developed into a thin hexagonal platlet (usually less than 1mm in thickness) with prismatic planes exposed. A number of stacking faults (S), as shown in Figure 1(b), were also observed and the fault planes are all (0001) planes. There is also direct evidence that one of the stacking faults (S1) is due to dissociation of a perfect dislocation into two partial dislocations (P).

Figure 1

† Acknowledgements: Work performed at the Stony Brook Synchrotron Topography Facility, Beamline X-19C, and supported by U.S. Army Research Laboratory (Adelphi, MD).

GROWTH DEFECTS IN LONGITUDINAL-CUT PVT 6H-SiC SINGLE CRYSTALS. †

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As a very important wide band-gap semiconductor material, SiC has many potential applications including high power devices, UV detectors and computer memories. However, growing large-size single crystals of high perfection seems to be very challenging. Currently, Physical Vapor Transport (PVT) is the only commercially viable process for growing 6H-SiC single crystal boules of over one inch in diameter. Defect structures, particularly dislocation structures, in (0001) 6H-SiC wafers grown in (0001) direction have been studied by using Synchrotron White Beam X-ray Topography (SWBXT) technique and the density of super screw dislocations along (0001) and glide dislocations in the basal plane is usually about 10^3 - 10^4 cm⁻² [1]. In the present work, several longitudinal-cut (i.e. cut parallel to the growth direction) 6H-SiC single crystals have also been examined by the SWBXT method. The topograph shown in Figure 1(a) is from part of a longitudinal-cut crystal wafer. The dark lines are super screw dislocations which follow the growth directions but deviate from (0001) by a few degrees, which means that these super dislocations are mixed-type. The faint lines nearly perpendicular to the super dislocations are obviously the glide dislocations confined in the basal plane. It should be noticed that some super dislocations terminate on a cluster of inclusions, as indicated by "I" on the enlarged topograph shown in Figure 1(b), and regenerate on the same inclusion cluster as crystal growth proceeds. Optical observations may give a wrong impression that the super dislocations terminate inside the perfect crystal due to the fact that very often the hollow cores of such super dislocations shrink as crystals grow, and optical microscopy has very limited strain sensitivity and very small depth of field. Another feature on the topographs is the small dense dark "dots", designated by "P". Some of the "dots" exhibit the typical "double-lobe" contrast and, therefore they are believed to be small inclusions or precipitates. Also, X-ray radiography shows that these "dots" are associated with some highly absorbing material, which suggests they may be Si-rich precipitates, though further investigations are still underway.

Figure 1

Reference: 1. S. Wang, M. Dudley, C. Carter, Jr., D. Asbury and C. Fazi, *Mat. Res. Soc. Symp. Proc.* **307**, 249 (1993).

† Acknowledgements: Work performed on the Synchrotron Topography Project Station, Beamline X-19C, and SiC single crystals are provided by Advanced Technology Materials, Inc., Danbury, CT.

COMPUTER AIDED ANALYSIS OF SYNCHROTRON WHITE BEAM X-RAY TOPOGRAPHS BY ADOPTING SPREADSHEET SOFTWARE. †

S. Wang, J. Wu, H. Chuang and M. Dudley (SUNY at Stony Brook)

Synchrotron White Beam X-Ray Diffraction Topography is a powerful technique for characterizing crystallographic defects in single crystals. Indexing the diffraction patterns recorded in either Laue transmission or Laue back-reflection geometries, is an essential step in analyzing the defects revealed by the X-ray topographs. Therefore, a computer-aided-analysis tool has been developed by adopting Spreadsheet software, such as Quattro Pro. The indexing scheme in the current program is similar to that of any other indexing codes, but the programming and debugging process is extremely straightforward simply because spreadsheet-type software is designed to be user-friendly. Another major advantage is the capability of displaying and printing graphs with a large enough range of magnifications. Figure 1(a) is an example of a transmission Laue pattern (for a (010)-cut KTiOPO₄ crystal) generated by using Quattro Pro, which can be compared with the pattern recorded experimentally, which is shown in Figure 1(b). On this computer generated pattern, the diffraction spots are labelled not only with (hkl)s, the reciprocal space vectors, but also the corresponding diffraction wavelengths (in Å) and μt values (where μ is the linear absorption coefficient and t is the crystal thickness), which are very crucial to the determination of diffraction contrast mechanisms and harmonic contamination in the images of interest. The program developed also has several rotation options, which simulate the experimental procedures of orienting the crystals on the goniometer. Further improvement of this analyzing tool can be readily achieved by incorporating the source spectrum and a structure factor calculation, so that the relative intensities of diffraction spots can be obtained directly.

Figure 1

† Acknowledgements: Topography work performed at the Stony Brook Synchrotron Topography Facility, Beamline X-19C and supported by E.I. du Pont de Nemours & Company, Inc.

X-19C

SYNCHROTRON WHITE BEAM REFLECTION TOPOGRAPHY OF INTERFACES IN GALLIUM-DOPED GERMANIUM. †

W. Zhou and M. Dudley (SUNY Stony Brook), C.H. Su, D.C. Gillies, F.R. Szofran and S.L. Lehoczky (NASA/Marshall Space Flight Center, Alabama).

The liquid-solid interface is one of the most fundamental parameters in crystal growth from the melt. Lack of control of the interface can lead to twin formation, enhanced nucleation and polycrystallinity, etc. There are several well established methods for interface demarcation, such as Peltier pulsing, mechanical vibration, setting temperature change, growth rate change and quenching-in the liquid. Initial testing of both the NASA Advanced Automated Directional Solidification Furnace (AADSf) and the Crystal Growth Furnace (CGF) was done with the sample consisting of germanium heavily doped with gallium. For the crystal grown in the AADSf, a technique involving resetting the cold zone temperature was employed. This crystal was done by stopping the growth, raising the cold zone temperature and then re-growing. For the crystal grown in the CGF, alternative methods such as mechanical pulsing were employed. Images of some of the interfaces in these two crystals are shown in Figures 1(a) and (b). One probable explanation is that due to the disturbance in the crystal growth procedure gallium dopant would be preferentially segregated at the interfaces and lead to local lattice disturbances. The local lattice strain leads contrast in X-ray topographs. By choosing proper diffraction conditions achieving the necessary strain sensitivity, the interfaces can be made visible.

† Acknowledgements: Work performed on the Synchrotron Topography Project Beamline X-19C, and supported by NASA Marshall Space Flight Center under Grant No. NAG8-891

X-19C

ATOMIC STRUCTURES OF TWIN BOUNDARIES IN ZnTe SINGLE CRYSTALS. †

W. Zhou and M. Dudley (SUNY Stony Brook), C.H. Su, M.P. Volz, D.C. Gillies, F.R. Szofran and S.L. Lehoczky (NASA/Marshall Space Flight Center, Alabama).

ZnTe single crystals used in this research were grown by horizontal physical vapor transport technique in a closed ampoule at NASA Marshall Space Flight Center. ZnTe twins easily on the {111} plane due to the fact that bonds across such a boundary are unstrained, leading to a minimum boundary energy compared to other possible boundaries. This kind of boundary is called a coherent twin boundary. Boundaries between twinned and matrix regions which laterally terminate twin lamellae are known as lateral twin boundaries. Due to orientation contrast, diffraction from twinned regions is shifted with respect to that from the matrix regions resulting in zero intensity regions. Fig. 1 shows part of a topograph ($g = 422$) from the crystal showing all segments of the twin boundaries, where LB represents lateral twin boundary and TB represents twin plane. There are two kinds of lateral twin boundaries observed in this crystal. They are $(\bar{1}\bar{1}2)$ and $(0\bar{1}1)$. Approximate atomic structures of the (111) twin plane and $(\bar{1}\bar{1}2)$ lateral twin boundary are shown in Figs. 2(a) and 2(b). In both cases, atoms are projected onto the (110) plane. As indicated in the diagram, the right hand side of the pattern represents the matrix region while the left hand side represents the twinned region. In the coherent twin boundary case the two regions are not mirror-image related. On the other hand, a $(\bar{1}\bar{1}2)$ lateral boundary is mirror-image related.

† Acknowledgements: Work performed on the Synchrotron Topography Project Beamline X-19C, and supported by NASA Marshall Space Flight Center under Grant No. NAG8-891

CORRELATIONS BETWEEN GROWTH DEFECTS AND GROWTH CONDITIONS IN ZnTe SINGLE CRYSTALS. †

W. Zhou and M. Dudley (SUNY Stony Brook), C.H. Su, M.P. Volz, D.C. Gillies, F.R. Szofran and S.L. Lehoczky (NASA/Marshall Space Flight Center, Alabama).

ZnTe is a potential material for optoelectronic devices operating at room temperature in the green spectral region. In order to investigate defects in this material, (111) slices were cut from a boule grown by physical vapor transport. Figure 1 shows a $(\bar{1}\bar{1}3)$ reflection, recorded in a geometry such that the diffraction wavelength was $0.45\text{\AA}$. This particular diffraction spot exhibits no orientation contrast from twinned regions, although some strain contrast associated with the twins can be discerned. An asymmetric distribution of slip dislocations between the $(\bar{1}\bar{1}1)$ and $(11\bar{1})$ planes can be observed, indicating that the thermal stresses that gave rise to the slip processes were not cylindrically symmetric. The cell structures to one side of the twinned regions are more well defined than the other and correspondingly the slip dislocation density on $(11\bar{1})$ is smaller in this same region of crystal. This is a direct result of the fact that slip bands, most of which were probably nucleated at the crystal edge, tend to break up the ordered cell structure leading to a somewhat linear structure. This could be evidence for the fact that the dislocation cell structure appears during the growth process, and that the slip dislocations appear later, perhaps during the cooling process. In addition, the uneven density of slip dislocations in matrix on both sides of the twin boundary possibly indicates that the twinning occurred before the generation of slip dislocations and that twin boundaries may act as barriers to slip. Thus, information on the growth history of a crystal can be inferred from simple analysis of X-ray topographs.

Fig. 1

† Acknowledgements: Work performed on the Synchrotron Topography Project Beamline X-19C, and supported by NASA Marshall Space Flight Center under Grant No. NAG8-891

PINNED AND UNPINNED STEP DYNAMICS ON VICINAL SILVER (110) SURFACES

G.A. Held, D.M. Goodstein, R.M. Feenstra (IBM Research Division), M.J. Ramstad, D.Y. Noh and R.J. Birgeneau (MIT)

A small density of steps may be incorporated onto a metal surface by deliberately cutting the crystal at an angle slightly off from a high symmetry direction. If the high symmetry surface does not reconstruct, the theory of equilibrium crystal shapes (ECS) predicts that at low temperatures the steps should either cluster together or spread uniformly across the surface. In the former case, a "hill and valley" structure of densely stepped rough regions coexisting with flat, high symmetry facets will result. The fraction of the surface comprised of flat facets should decrease with increasing temperature, falling to zero at some temperature below the roughening transition temperature of the facet. In the latter case, the surface is predicted to be rough at all temperatures.

We have carried out x-ray scattering and scanning tunneling microscopy (STM) studies of a Ag(110) sample miscut 1° from the $[110]$ axis along the $[1\bar{1}0]$ direction. For a clean and well annealed surface, we find that at all temperatures above 300 K the surface is comprised of a uniform density of single atomic height meandering steps (Fig. 1). That is, we find no evidence for vicinal phase separation. However, as the surface is annealed to sufficiently high temperatures, we find that impurities are driven to the surface and that this, in turn, results in the formation of large, flat (110) terraces, as may be observed in Fig. 2. For the clean surface we observe diffraction characteristic of uniform, albeit meandering, steps at all temperatures between 300 K and 875 K. With increasing temperature, the step peaks lose intensity and undergo an evolution in lineshape consistent with a decrease in step-step correlations, most noticeably in the $[001]$ direction. While our data above 670 K are consistent with a rough surface, the peak evolution is not consistent with the simplest model of entropically repulsive steps.

Fig. 2. Scans of the $(0.05\ 0.05\ 1)$ surface peak position after a 4 hr anneal at 873 K. Scattering from both impurity pinned terraces (central peaks) and stepped regions of the surface (shoulders on the peaks) may be observed. The momentum transfer q measures the displacement in rlu from $(.05\ .05\ 1)$ along the $(1\bar{1}0)$ miscut direction.

Fig. 1. Scans of the clean surface at the $(0.98\ 1.02\ 0)$ position. (a) and (c) are scans along the $(1\bar{1}0)$ miscut direction while (b) and (d) are along (001) (transverse to the miscut), through the centers of the peaks at positive q in (a) and (c), respectively. Units are rlu $\equiv 2\pi/a_0$.

RANDOM FIELD DYNAMIC ROUNDING IN $\text{Fe}_{0.5}\text{Zn}_{0.5}\text{F}_2$

X20A

J.P. Hill, T.R. Thurston (BNL), Q. Feng, Q.J. Harris and R.J. Birgeneau (MIT)

As an example of a phase transition in the presence of disorder, the random field Ising model has been much studied over the previous two decades. The most convenient realizations of this model are the dilute antiferromagnets in a field (DAFF's). Traditionally, the sub-lattice magnetization has been studied with neutron scattering. However the magnetic peaks are extinction limited in these high quality crystals and measurements of the order parameter are not trustworthy. Magnetic x-ray scattering offers a high resolution, extinction free measurement of the order parameter. In addition, the small penetration depth reduces effects due to concentration gradients.

The DAFF's are known to be highly hysteretic below a metastability temperature $T_M(H)$. A domain state is formed for $T < T_M(H)$ on cooling in a fixed field. If however the sample is cooled in zero field, and a field subsequently applied (ZFC) then magnetic LRO is achieved. We have used magnetic x-ray scattering to study the evolution of the ZFC LRO state in $\text{Fe}_{0.5}\text{Zn}_{0.5}\text{F}_2$ on warming. The order parameter data are well described by a power-law-like transition with an exponent $\beta = 0.13 \pm 0.05$. The transition region is broadened and may be described by a Gaussian distribution of transition temperatures, centered at $T_c(H)$, of width $\sigma_{ZFC}(H)$. It is found that $\sigma_{ZFC}(H) = AH^2$. This rounding is attributed to extreme critical slowing down, which prevents equilibrium being attained for experimental time scales. Complementary neutron scattering studies on the same sample allow identification of the center of the Gaussian distribution, $T_c(H)$, with the temperature at which the correlation length saturates.

X20B

X-RAY REFLECTIVITY AS AN IN-SITU PROBE OF SURFACE MODIFICATIONS OF POLYIMIDE FILMS UNDER WET CHEMICAL PROCESSING

C. Thompson (Polytechnic University), R. Saraf and J. Jordan-Sweet (IBM)

Understanding the structural and chemical changes which occur at the surface of polymer films during chemical processing has important technological implications. It is difficult to observe surface structural changes during the processing. There exist, therefore, many unanswered fundamental questions about the kinetics of the processing, the extent to which the surface is altered while in solution, and the coupling of surface and interface morphological changes to the chemical changes. We are using x-ray reflectivity and related techniques to probe in-situ the changes of the surface of thin polyimide films during chemical surface modification steps which are used to obtain Pd clusters on the polymer surface for subsequent electroless plating of copper. We are measuring the changes in time for the reflectivity for the 1.) activation of the polyimide surface under NaOH, in which both Na ions diffuse into the polymer and a ring opening reaction is initiated to form an Na-PI salt, 2.) ion exchange of Pd ions with the Na ions, 3.) the reduction of the Pd ions, and 4.) the migration of the Pd atoms to form clusters. The studies were carried out on PMDA-ODA polyimide.

X-RAY SCATTERING STUDIES OF $\text{SiO}_x/\text{Si}/\text{Ge}(001)$

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X-ray scattering has been used to study the structure of strained silicon/silicon oxide interface. The sample is composed of four monolayers of Si epitaxially deposited on a Ge(001) substrate; the sample was then oxidized in dry oxygen at room temperature.

Specular reflectivity data along with a theoretical fit are shown in figure 1. The model profile of the average electron density perpendicular to the surface that results from this fit is shown in the inset of figure 1. The model consists of an abruptly terminated Ge(001) substrate, five intermediate layers and an amorphous oxide overlayer, which permeates into the upper two intermediate layers. GID studies show that the surface is miscut by 0.13 deg from the (001) surface. The density of layers 1-3 is within 10% of bulk Ge. Together with the fact that unoxidized Si was observed in XPS measurements, we assume that these layers consist of intermixed $\text{Si}_y\text{Ge}_{1-y}$. Layers 4 and 5 are the transition from Ge to Si, and then to the oxide. The thickness of the amorphous oxide overlayer is about 10 Å, which is about twice of the thickness of the amorphous oxide layer observed on a similarly prepared Si substrate¹. Its density is 115% that of bulk SiO_2 . XPS data indicates that there is some GeO_x near the surface region. This suggests that oxidization of the Si is not complete and that there is some Ge in the oxide layer.

Squares in figure 2 display the data of the $(-1\ 1\ q)$ crystal truncation rod collected from the same sample. The calculated result (solid line) is the specular model with additional parameters to describe the Debye-Waller factor associated with the in-plane disorder of the intermediate layers, and shows a reasonable fit. The discrepancy between the experimental data and the calculated values near the anti-Bragg point is possibly due to lateral deformation of the intermediate layers.

¹ T.A. Rabedeau, I.M. Tidswell, P.S. Pershan, J. Bevk and B.S. Freer, Appl. Phys. Lett. **59**, 3422 (1991).

Figure 1. Specular reflectivity data ($\square$) and fit (—) for the oxidized Si on Ge(001) sample. Inset: electron density normal to the surface.

Figure 2. $(-1\ 1\ q)$ crystal truncation rod data ($\square$) and fit (—)

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GIANT MAGNETORESISTANCE AND Co CLUSTER STRUCTURE IN PHASE SEPARATED Co-Cu GRANULAR ALLOYS.

T.A. Rabedeau, M.F. Toney, R.F. Marks, S.S.P. Parkin, R.F.C. Parkin, and G.R. Harp (IBM Almaden)

The recent observation of giant magnetoresistance (MR) in granular alloy films, which are composed of magnetic clusters embedded in a non-magnetic metal matrix, has stimulated considerable research into the MR in these materials.¹ These films are typically fabricated by codeposition of two immiscible metals such as Co and Cu and then annealed to promote phase separation and cluster growth. Analogous to MR in multilayers, the resistance of granular films depends upon the distribution of magnetic moments of the magnetic clusters with parallel alignment of the moments yielding the minimum resistance. This dependence of the resistivity is attributed to spin dependent electron scattering occurring within the ferromagnetic clusters and/or at the magnetic non-magnetic interfaces. Both phenomenological theory and experimental results indicate that the MR depends critically on the film structure; however there has been little structural characterization of alloy films exhibiting MR.

We investigated the relationship between cluster structure and MR using grazing incidence, anomalous, small angle x-ray scattering (SAXS) to probe clustering in thin $\text{Co}_{16}\text{-Cu}_{84}$ films formed by molecular beam epitaxy on sapphire substrates. Five films were deposited simultaneously at 200°C and subjected to differing post-growth thermal anneals. The as-grown films exhibited the maximum MR, 35%, while the film annealed at the highest temperature (10 minutes at 550°C) displayed only 1% MR. (MR is defined as $R(H) - R(H_{sat}) / R(H_{sat})$ where R is the film resistance and H is the applied magnetic field with H_{sat} denoting the saturation field.) SAXS data indicate that the decreasing MR is accompanied by a concomitant increase in Co cluster diameter. Explicitly, the MR scales approximately as the inverse cluster size (see figure). This scaling relationship indicates interfacial spin dependent scattering is the dominant scattering mechanism underlying MR, since spin dependent scattering in the interior of the magnetic clusters should be relatively independent of cluster size while interfacial scattering should be proportional to interfacial area which scales as the inverse cluster diameter. Comparison to phenomenological theory² permits quantification of the relative importance of volume vs. interfacial spin dependent scattering and confirms the dominance of interfacial scattering.

¹ A.E. Berkowitz, et al., Phys. Rev. Lett. **68**, 3745 (1992); J.Q. Xiao, et al., Phys. Rev. Lett. **68**, 3749 (1992).

² S. Zhang, Appl. Phys. Lett. **61**, 1855 (1992).

MR vs. the cluster radii (Porod radii) extracted from the SAXS data. The solid line depicts a fit to the data using the theory of Zhang.² The fit indicates the ratio of the down-spin to up-spin scattering lengths is 10 at the interfaces and 1 in the interior of the magnetic clusters.

X20C

THERMAL EXPANSION MEASUREMENTS OF THIN FILM POLYIMIDES AS A FUNCTION OF THICKNESS AND AS A FUNCTION OF PRECURSOR BLEND RATIO

R. Saraf, G.B. Stephenson, J. Jordan-Sweet (IBM), C. Thompson (Polytechnic University)

The structure of polyimide in proximity to the interface is different than the bulk. Results in the literature using surface x-ray diffraction have shown an enhanced crystallinity at the surface of thin films. It is expected that the morphology of the structure is highly anisotropic. It may be expected, therefore, that the physical properties of thin films may depend on thickness, and that they will differ from the bulk.

Using X-ray reflectivity, we have measured the thermal expansion coefficient for three thicknesses of cured PMDA-ODA polyimide films made from an ester (PAETE) precursor (40nm, 110nm, and 260nm), and for a cured film (118nm) made from an acid/ester precursor blend in 1:1 ratio. The blend due to its microstructure, may have properties which are not as anisotropic as the conventional spin-coated films made from single precursors. Prior to the measurements, the samples were stored in a desiccator to avoid moisture absorption. For the reflectivity measurements, the samples were mounted in a vacuum furnace and reflectivity profiles taken at room temperature and at 200degrees centigrade, which is below the glass transition for these samples. It was found that it was necessary to cycle once to the 200degree temperature, for subsequent reflectivity profiles to be reproducible and reversible with temperature.

Although we are in the process of completely analyzing the profiles and results, initial estimates for the thermal expansion coefficients show an increase with increasing thickness of the films from an approximate $55 \times 10^{-6}/\text{degC}$ for the 40nm film to an estimated $160 \times 10^{-6}/\text{degC}$ for the 260nm film. The coefficient of the 1:1 PAETE/PAA blend was approximately 70percent of the coefficient for the 110nm PAETE film of $130 \times 10^{-6}/\text{degC}$. It should be noted that in this experimental configuration, the thickness change measured will not be the linear thermal expansion coefficient because the thin film is constrained in the lateral dimension due to adhesion to the silicon substrate.

X20C

NUCLEATION OF THE BCC PHASE IN ASYMMETRIC DIBLOCK COPOLYMERS.

R. F. Shannon, Jr. and M. A. Singh. (Queen's U.)

Time resolved small-angle-x-ray-scattering has been used to study nucleation and growth in diblock copolymers. Anionically polymerized styrene-butadiene (30.5 wt.% styrene, $M_w = 5.22 \times 10^4$) mixed with the selective solvent, n-tetradecane, was examined under thermal quench conditions. The growth of the ordered microdomain regions in samples doped with $0.3 \mu\text{m}$ sized particles of alumina is compared to that in pure samples. The growth of the ordered volume fraction (OVF), which is proportional to the amplitude of the primary Bragg peak (see figure), takes place on a longer time scale with a different functional form in the pure sample as compared to the doped sample. The data has been fit by three models; heterogeneous nucleation at two dimensional surfaces (2D-Cahn); heterogeneous nucleation at point sites (pt-Cahn); and the standard Mehl-Johnson-Avrami (MJA) model for constant volume nucleation and isotropic growth. In the case of the doped samples the pt-Cahn model provides a good description of the kinetics. The 2D-Cahn model's ability to fit the pure sample data shows the difference in the functional form between the two. The MJA growth exponent according to the model is 4.0 ± 0.3 for the pure case, indicating a constant rate of nucleation, and 1.9 ± 0.3 for the doped sample, indicating a decreasing rate. For both samples the equilibrium OVF was the same and less than one. Comparisons to previous work¹, which resulted in 50% greater OVFs, suggest that the observed equilibrium coexistence (amorphous vs. crystalline phases) is the result of a non-negligible strain energy caused by a volume constraint combined with expansion of the sample upon crystallization. Experiments using a constant pressure cell will allow complete ordering and observation of domain coarsening effects.

¹C. Harkless et al., Phys. Rev. Lett. 64, 2285 (1990).
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DISTRIBUTION OF WATER MOLECULES AT THE SILVER(111)-ELECTROLYTE INTERFACE

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The spatial distribution of water molecules at solid-electrolyte interfaces is quintessential to electrochemistry, geochemistry, and biology. This structure has been the subject of extensive theoretical work,¹⁻⁸ and it is generally believed that the water is ordered in layers extending several molecular diameters from the interface. There are also suggestions that the first water layer adopts an ordered 'ice-like' structure driven by hydrogen bonding. The water structure depends on the charge of the interface (or applied potential), and it is expected that the average orientation of water molecules in the first layer changes from oxygen-down for positive electrode charge to oxygen-up for negative charge with, respectively, a smaller (larger) water-electrode spacing. Despite these extensive theoretical studies, there have been few experimental measurements of the molecular arrangements.

To obtain insight into the water structure, we have measured the non-specular and specular truncation rods from a silver (111)-electrolyte interface in 0.1 and 0.002M NaF at +0.52V and -0.23V from the potential of zero charge on the electrode (pzc). Analysis of the non-specular rods shows that at the positive potential, the spacing between the topmost and second Ag(111) planes is contracted relative to the bulk spacing (by about 0.03 Å), while at the negative potential, this spacing is the same as in bulk. Such an effect has not been observed or predicted before, but can be qualitatively explained as follows: a positive surface charge tends to reduce the extent the metal electron density extends beyond the surface and this pulls the topmost Ag ion cores toward the second Ag(111) plane (e.g., contraction). An opposite argument applies for a negative surface charge.

The water distribution perpendicular to the electrode was obtained from the specular truncation rod data. We find that, first, the water is ordered in layers extending about three molecular diameters from the electrode, and second, the distance between the electrode and first water layer is larger at -0.23V than at +0.52V. Both of these observations are consistent with the ideas outlined above. However, the areal density in the inner layer is enormous: 1.1 (-0.23V) and 1.8 (+0.52V) water molecules per Ag atom. One expects, based on the bulk water density, 0.7 molecules per Ag atom. Thus, the water molecules in the inner layer are significantly compressed! This is a crucial component of the water distribution that has not been predicted or observed in previous work. It implies that the distribution is determined by more complicated factors than simple steric packing and that the hydrogen bonding in liquid water is not maintained in the inner layer. Furthermore, an 'ice-like' structure does not exist at the potentials we have investigated.

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GRAZING-INCIDENCE X-RAY SCATTERING STUDIES OF THIN FILMS OF PERFLUOROPOLYETHER.

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Perfluoropolyethers (PFPE) form an important class of thin film lubricants. Yet, there is virtually no knowledge of the molecular ordering of such polymers in thin films nor of the relationship between ordering and lubrication. We have used grazing-incidence X-ray scattering to investigate the order of PFPE films with thicknesses between 10 and 110 Å. The PFPE (Demnum SP-65) are linear chain molecules with an end-to-end length of about 120 Å and a thickness of about 7 Å. We find that the X-ray scattering is essentially independent of the film thickness and is also the same whether the scattering vector is parallel in the substrate surface or has a significant component perpendicular to the surface (asymmetric Bragg geometry). This surprising result means that even for films as thin as one to two molecular diameters there are no substantial differences in polymer ordering as a function of film thickness and that this ordering is essentially isotropic.

Using the usual methods, we have calculated the radial distribution function (RDF) for a 100Å PFPE film and this is shown in the Figure. The first peak (at 1.4Å) is due to intermolecular scattering (e.g., C-C, C-F); the peaks at larger r are due to intramolecular scattering and we are in the process of understanding these. The RDF's from PFPE films with different thickness will be the same, to within experimental error. Our results demonstrate that X-ray scattering can be used to study the ordering in thin, poorly ordered polymer films.

Radial distribution function from a 100Å PFPE film.

X-RAY SCATTERING STUDY OF CHARGE DENSITY WAVE RELAXATION

J. Zhang, J.F. Ma, S.E. Nagler (U. of Fla.) and S.E. Brown (UCLA)

We have studied the relaxation of the charge density wave (CDW) lattice upon application of a dc electric field at 19 K by x-ray scattering. Fig. 1 shows the time dependence of the scattering intensity, a quantity which measures the number of photons scattered into a certain region near the CDW peak position (13,0.7485,-6.5) in reciprocal space. Fig. 2 plots the intensity of Fig. 1 vs. the electric current that is measured in-situ. A clear one to one correlation is present between the structural change and the transient of the electrical transport property except for the first few points which lasted for about 20 sec. The explanation for the lack of correlation in the beginning and a detailed discussion of the relaxation kinetics are presented in a paper [J. Zhang, et al., PRL 70, 3095].

Fig. 1 Time evolution of the CDW peak intensity after a dc electric field of 25 V/cm was applied.

Fig. 2 CDW peak intensity vs. electric current measured in-situ after a field of 25 V/cm was applied at 18.9 K. The line shows the correlation.

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The Electrodeposition of Pb Monolayers on Low Index Pt Surfaces

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The electrodeposition of a lead monolayer on Pt(111) in HClO_4 solution forms an ordered structure with a rectangular $4\text{Pb}-(3 \times \sqrt{3})$ unit cell, $\theta_{\text{Pb}}=2/3$, as determined by *in situ* x-ray glancing angle diffraction and x-ray reflectivity techniques. No ordered structures were observed for Pt(100) and Pt(110). Ordered adlayer structures have been found at potentials close to reversible bulk deposition only on Pt(111). An order-disorder transition appears to result in a sharp peak observed in the cyclic voltammetry curve for Pb monolayer formation on a well-ordered Pt(111) single crystal surface in 0.1 HClO_4 containing 5mM Pb^{2+} (Fig. 1a). The in-plane diffraction data show three rotationally equivalent domains of a centered-rectangular diffraction pattern from the lead adlayer. The real space model derived from the diffraction pattern has four Pb atoms in a rectangular $(3 \times \sqrt{3})$ cell as shown in Fig. 1b. The Pb coverage calculated from this structure, $\theta_{\text{Pb}}=2/3$, is slightly higher than the coverage of 0.63 predicted for a hexagonal close-packed Pb monolayer. The observed Pb adlayer is uniaxially compressed relative to a hexagonal phase; distances between four of the six neighboring Pb atoms are 3.18 Å and between the remaining two the distance is 4.81 Å. The latter distance is commensurate with the $\sqrt{3}$ spacing for Pt(111). Results from fitting the reflectivity curves, using simple density profiles, yields a Pt-Pb layer spacing of 2.34 Å and a Pb coverage of $\theta_{\text{Pb}}=0.65 \pm 0.05$. This coverage is in excellent agreement with the $2/3$ coverage calculated for the $4\text{Pb}-(3 \times \sqrt{3})$ structure.

It is noteworthy that the adlayer of Pb formed on Pt(111) is commensurate. Only incommensurate hcp layers were found on Ag(111) and Au(111). Also noteworthy, ordered adlayers were found on Ag and Au for all adsorbates investigated thus far, contrary to the present results for Pt. Lack of ordered structure in the Pb adlayer on Pt(100) and Pt(110), compared with ordered structure on Pt(111), is particularly interesting. This is probably due to a stronger adatom-substrate interaction for Pt(100) and Pt(110) compared with Pt(111).

The present results also indicate that *ex situ* determination of adlayer structures may not be relevant to electrochemical conditions because of a loss of potential control in UHV. Ordered Pb adlayer structures determined on Pt(100) could not be confirmed in this work. These results emphasize the importance of the *in situ* studies of electrodeposited monolayers.

(a) Diffraction Pattern

(b) Real Space Model

Phase Behavior of a Monolayer of Behenic Acid at the Air-Water Interface, as Determined by Grazing Incidence X-ray Diffraction.

G. M. Bommarito, W. J. Foster, P. S. Pershan (Harvard University), and M. L. Schlossman (University of Chicago)

Grazing incidence x-ray diffraction (GIXD) measurements were carried out on a Langmuir monolayer of behenic acid ($C_{22}H_{44}O_2$) between 2 and 18 °C and a subphase pH of 2.0 (HCl buffer). The morphologically rich phase diagram of this fatty acid was mapped out using two different methods. In the first, the structural changes in the monolayer were followed, via the x-ray diffraction measurements, as a function of what we have termed "relaxation" isotherms. These relaxation isotherms consist of a series of small compression steps, allowing the monolayer's surface pressure to attain an equilibrium value after each change in area. Because of this compression mode, we observe isotherms that differ considerably from measurements in which the film is compressed continuously at a given rate. These differences produce an equilibrium phase diagram that is qualitatively similar to published phase diagrams of similar systems, however, there are significant quantitative differences.

Describing qualitatively this phase diagram (see figure), we observe four distinct phases between 2 and 12 °C and over a surface pressure range of 0 to 15 dynes/cm. At the high end of the temperature range and at low pressures we find the I phase. This phase has distorted triangular order with a molecular tilt toward the nearest neighbor. For high temperatures and high pressures we observe the F phase. This phase also has distorted triangular order but a molecular tilt toward the next nearest neighbor. At lower temperatures (< 9°C), the transition between the I and F phases exhibits a discontinuous change in the unit cell area. However, at higher temperatures the unit cell area difference between the two phases, upon the transition I to F, becomes negligible. The I' phase is at the lower end of the temperature range and at low pressures. This phase has the same symmetry and tilt order of the I phase, but a smaller unit cell area, and the I to I' transition is always first order. Finally, at low temperature and high pressures we observe an untilted phase (U phase), with a first order U to F phase transition.

To better understand the differences noted in this phase diagram when compared to published data, we observed structural changes while varying only the temperature of the film at a fixed trough area. These measurements confirmed that the I' to F transition is first order and occurs at approximately 5.6 °C, independent of surface pressure. In addition, measured thermodynamic quantities such as latent heats are extracted from the structural data using thermodynamic relations.

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Study of the X-ray Critical Scattering in SrTiO₃

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We have studied X-ray critical scattering above the zone boundary structural phase transition in two single crystals of SrTiO₃. Earlier studies have suggested two length scales in the critical scattering; a second sharper component in addition to broad one expected by soft mode theory. Our results, however, show only the narrow component in the two samples in spite of careful measurements and analyses. In contrast, the neutron scattering on the same samples exhibit only the broad component. Taking account of recent study of another two length scale phenomenon in Tb [1], we think that, in our samples, the skin phase accommodating the narrow component is thick enough to prevent penetration of X-rays, whereas not enough to appear in neutron scattering.

We analyzed the narrow component by fitting the data with a Lorentzian squared model, convoluted with the instrumental resolution. As shown in figure 1, the temperature dependence of the narrow component is in good agreement with one of the earlier studies [2]. Figure 2 shows the amplitude of the Lorentzian squared component. One of the samples (Sanders) provides a order of magnitude higher intensity than the other (Fujii), though both show a power law like behavior. For that reason, we could observe the critical scattering up to $T_c + 30K$ in the former sample. This discrepancy is probably due to difference of the skin thickness.

Figure 1.

Figure 2.

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[2] D.F. McMorro *et al*, Solid State Commun. **76**, 443 (1990)

Critical fluctuations in the quasi-one-dimensional semiconductor (NbSe₄)₃I.

J.E. Lorenzo and T. Thurston (BNL)

(NbSe₄)₃I belongs to the family of transition metal tetraselenides with general formula (MSe₄)_nY (M = Nb or Ta; n = 2, 3, 10/3 or 4, for the known stable compounds and Y = I or Br). The structure consists of (MSe₄)_∞ chains aligned parallel to the c-axis and separated from one another by iodine atoms. Each metal atom is sandwiched between two rectangular selenium units, each consisting of two Se₂⁽⁻²⁾ dimers, rotated by an angle of about 45 degrees. The role of iodine atoms is to keep the chains together by attracting and canting the selenium dimers with respect to the basal plane. The physical properties of all the compounds are mainly determined by the metal-metal distances along the chain. At room temperature, (NbSe₄)₃I has space group P4₂/mnc (Z = 4) and lattice parameters: a=9.489 Å and c=19.13 Å. At T_C=273 K it undergoes a ferrodistorive phase transition to space group P4₂/c. The symmetry loss at T_C uniquely determines the irreducible representation of the order parameter, namely B_{1u} (Raman and infrared inactive). In contrary to the rest of compounds of this family which exhibit a metal-insulator phase transition with the opening of a gap at the Fermi level and the formation of an incommensurate charge density wave (ICDW), (NbSe₄)₃I can be considered as a built-in commensurate CDW. The origin of the phase transition at 273 K remains unknown. Previous inelastic neutron scattering studies at the phase transition revealed the presence of a central peak, whose intensity diverges at T_C, and a small softening of the appropriate phonon mode coordinate. The phonon branch is nearly flat in the basal plane and very steep along the chain direction. The frequency of this mode is very small above T_C and undergoes a strong renormalization below T_C. The elastic and the inelastic experiments showed that the

q-dependence of this central peak corresponds to that of the phonon branch. Previous x-ray studies on this compound were performed with a rotating anode and reported a correlation length of fluctuations 4 times bigger than that measured by neutrons. It is then natural to double-check the x-ray results. We did the experiments at the same Q-position as previous neutron experiments (and conventional rotating anode), which is the most intense new Bragg peak of the low temperature structure: Q = (3 0 6). In the figure we have plotted scans along the a* direction at 2 temperatures. From this figure we can clearly appreciate the presence of 2 components, the broadest one corresponding to that observed in our previous neutron experiments while the narrowest is that of previous x-rays rotating anode experiments. The results of this experiment have to be placed in the context of previous experiments performed at NSLS concerning the presence of 2 central peaks (KMnF₃, Ho, Tb, UO₂ etc). New high resolution neutron scattering experiments are under way.

AN X-RAY REFLECTIVITY STUDY OF THERMAL CAPILLARY WAVES ON LIQUID SURFACES

B. M. Ocko (BNL/Physics); X. Z. Wu, E. B. Sirota, S. K. Sinha (Exxon); and M. Deutsch (Bar Ilan U.)

Since the pioneering microscopic theory developed by van der Waals one hundred years ago it has been realized that the liquid-vapour interface is not atomically sharp, rather it is gradual and continuous. The gradual nature of the interface is also apparent from the capillary wave model which is an extension of the macroscopic elasticity theory to microscopic lengths. Within the context of the capillary wave model, the interfacial width is calculated by integrating the thermally excited capillary spectrum from the gravitational cutoff (1 cm) to an atomic scale, short wavelength cutoff (q_{max}). Despite these theoretical efforts the exact origin of q_{max} and the subsequent interfacial width remains controversial.

X-ray reflectivity measurements have been carried out at the liquid/vapour interface of normal alkanes. As the temperature is increased, the surface tension decreases (see Fig. 2 insert) and the combined effect increases the capillary wave roughness. This has the effect of decreasing the x-ray reflectivity, at fixed q (see Fig. 1). The reflectivities over a large temperature range of different chain lengths (C20 and C36) provides a critical test of several different capillary wave models. Our data is most consistent with the hybrid model which allows for a temperature independent molecular size dependent cut-off q_{max} for the capillary waves and an intrinsic interface width $\sigma_0 = 1.1 \text{ Å}$.

Figure 1. The reflectivities of C20 at T = 40, 70, 100, 130°C versus q_z . The reflectivities decrease more rapidly with q_z for the higher temperatures. The lines are the fits. In the insert, the reflectivities normalized by the Fresnel Reflectivity (R_F) are plotted as a function of q_z^2 .

Figure 2. The effective roughness σ_{eff} of C20 and C36 are plotted as a function of temperatures. The inset shows the surface tension γ of C20 and C36.

A STUDY OF SUBSTRATE-INDUCED ALIGNMENT IN A SMECTIC LIQUID CRYSTAL: EFFECTS OF TEMPERATURE CYCLING

Elisabeth Smela and L. J. Martínez-Miranda (U. of Penn.)

We performed a structural x-ray study on smectic 8CB films where the thickness of the films was changed systematically from 6 μm through 42 μm . The films were deposited on gratings with a 664 nm, 9 μm , 15 μm and 200 μm repeat distance. The purpose of our measurements was to investigate the onset and evolution of parallel alignment as a function of film thickness, and how grating repeat distance influences it.

The experiments used 9 keV (1.403 Å) x-rays, focused on a spot of 2 mm² at the sample position. The detector slits were kept at a 10(vertical) x 4(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 $\mathbf{l}$ in reciprocal space. We performed these scans at angles corresponding to directions along the gratings ([011] direction) as well as directions perpendicular to the gratings ([101] direction). The diffraction angles $\theta, 2\theta$ were held constant at the Bragg value for 8CB. At $\chi = 90^\circ$, the observed scattering corresponds to smectic layers parallel to the surface of the gratings (molecules perpendicular to the plane of the substrate). Conversely, at $\chi = 0^\circ$, 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° for 9 keV x-rays. Finally, we performed azimuthal ϕ -scans at $\chi = 0^\circ$ and $\chi = 10^\circ$ in order to observe the degree of in-plane disorder. For these scans, $\phi = 0^\circ$ corresponds to the [011] direction. We fit our results to a multilayer model where the orientation of the smectic layers varies as a function of film depth¹.

We summarize our results as follows: The cooling rate, and the cooling procedure, which allows the molecules to respond to the influence of both the air and the substrate surfaces, play an important role in the alignment of the LC molecules, and influences the degree of disorder of the homogeneous layers. The azimuthal ordering of fast cooled films was very broad, exhibiting low reproducibility. Films that were cooled using a slow cycling method, such as that obtained when heating the sample from the side, showed a high degree of orientation along the grating direction. These films appeared very uniform when observed under a microscope; only those defects associated with the rotation of the LC molecules at the edge of the gratings could be observed. However, we note that the cooling rate *does not* affect the measured layer thickness, as can be observed in Figure 1. Finally, the analysis suggests that the transition layer between the homeotropic and homogeneous layers is a very sharp one.

The degree of order and layer thickness observed in gratings with periods of 9, 15 and 24 μm is similar to that obtained from gratings with period of 664 nm, prepared using laser lithography. The LC does not align in gratings larger than 200 μm ; the preliminary analysis of LC films on a 200 nm period grating seem to show a similar behavior. Thus our studies appear to indicate both upper and lower limits to the alignment of LC films between strong and weak aligning surfaces, which can prove useful in the future applications of such films in sensing devices.

¹Elisabeth Smela and L. J. Martínez-Miranda, J. Appl. Phys., 73, 3299-3304 (1993); E. Smela and L. J. Martínez-Miranda, Liq. Cryst., 14, 1877-1883 (1993).

Figure 1. Summary plot showing layer thickness as a function of 8CB liquid crystal film thickness.

This work was partially supported by NSF Grant No. ECS-92-01986, and by the NLS Faculty-Student Support Program.

Electrochemical Deposition of Tl Monolayer on Au(111) in Alkaline Solution: Rotational Phase Transition and Coadsorption of OH⁻ Anions

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The structure of Tl monolayers on the Au(111) in alkaline solution was determined as a function of the potential by in situ x-ray glancing angle incident diffraction technique. Previous electrochemical studies have shown the catalytic effect of the Tl monolayer on oxygen reduction. However, the relationship to the Tl monolayer structure was not known. The current response to the linear potential sweep of 2 mV/s in 5 mM Tl + 0.1 M NaOH is shown in the top panel of the figure. Just below the gold oxidation potential, a pair of Tl oxidation-reduction peaks occurs around -0.1 V indicating the existence of adsorbed Tl below this potential. The oxygen reduction switches between the four- and two-electron transfer processes around -0.4 V where there are two reversible current spikes.

The Tl monolayer exhibits a rotated-hexagonal phase from -0.66 V (just short of the bulk deposition potential) to -0.38 V. The Tl-Tl separation in this incommensurate phase changes with potential continuously from 3.34 to 3.43 Å. The later is the averaged Tl-Tl separation in the bulk crystal. The rotation angle of Tl monolayer with respect to the substrate varies with the incommensurability between 5.3-6.3° in a qualitative agreement with the McTague-Novaco-theory.

As the rotated-hexagonal phase vanished above -0.38 V, the aligned-hexagonal diffraction pattern appeared at -0.36 V. The sharp rotational transformation was accompanied by a discontinuous change of Tl coverage from 0.71 to 0.55 in number of Tl per gold surface atom. The charge associated with the larger current spike agrees with this coverage change of 0.16. The smaller current spike is likely to be a consequence of the double layer charging due to the formation of the OH⁻ coadsorbed phase. The Tl-Tl separation in the aligned-hexagonal phase ranges from 3.82 to 4.12 Å, which leaves room for OH⁻ adsorption. Therefore, the four-electron transfer reduction of oxygen is related to the interaction of oxygen containing species with Tl and gold. This is the first example of an incommensurate phase formed at low coverage in the electro-deposited adlayers studied so far. This work demonstrates that anion coadsorption can induce ordering of an adlayer without being commensurate with the substrate.

A NEW SURFACE PHASE IN LIQUID NORMAL-ALKANES

X. Z. Wu, E. B. Sirota, S. K. Sinha (Exxon); B. M. Ocko (BNL/Physics); and M. Deutsch (Bar Ilan U.)

X-ray grazing incident-angle diffraction and reflectivity measurements have shown that a crystalline, single molecule thick alkane film forms on the surface of bulk alkane liquids at temperatures up to 3 °C above the bulk solidification temperature, T_f . Whereas previous measurements were carried out for chain lengths of 18, 20 and 24 carbons only[1], the present measurements were carried out for the full range of lengths between 14 and 50[2,3]. The modulated reflectivity profiles for $T > T_f$ provide information on the density and layer thickness (Fig.1). A single solid monolayer persists down to T_f , thus exhibiting a very limited partial wetting. In-plane diffraction measurements have shown that the molecules in the monolayer are hexagonally packed and oriented normal to the surface. The layer thickness D and the in-plane lattice spacing d are plotted as a function of carbon number n in Fig.2. The new surface phase is obtained only for chain lengths $16 \leq n \leq 50$. These results are in good agreement with surface tension measurements[2]. The absence of the surface phase for $n \leq 14$ is interpreted as a possible transition from surface freezing to surface melting behaviour.

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Figure 1. X-ray reflectivities for C36, in the liquid surface phase (circles) and the surface monolayer phase (squares). The solid lines are fits to the data.

Figure 2. (a) The reflectivity-measured monolayer thickness D . (b) The in-plane lattice spacing d of the hexagonally packed surface monolayer.

MAGNETIC AND STRUCTURAL BEHAVIOR OF SINGLE CRYSTAL SAMARIUM.

E.M. Forgan (Birmingham U. U.K.), W.J.Nuttall, W.G. Stirling (Keele U. U.K.) and M.M.R. Costa (U. Coimbra, Portugal).

We have continued our investigation into the magnetic structure of samarium which is known to be a c-axis antiferromagnet with the unusual ABABCBAC structure of close packed hexagonal layers [1]. Samarium is particularly difficult to study experimentally despite its importance as a light lanthanide element. Neutron studies are hampered by the very large absorption cross-section while X-ray studies are technically challenging given the extremely small moment ($\sim 0.1 \mu_B$ at zero wavevector). The most important previous scattering study has been a neutron experiment using an isotopically enriched sample [2].

Our experiment utilized a solid state detector to improve signal to noise (achieving $I_{\text{sig}}/I_{\text{noise}} \sim 2.4$) by reducing the fluorescence signal and a closed cycle Joule-Thompson helium refrigerator in order to investigate very low temperatures.

We have obtained improved measurements of the resonant spectra as a function of energy near the L_{III} edge [Fig. 1.], and to a lesser extent the L_{II} edge. We have measured the (0, 0, 7.5); (0, 0, 10.5); (0, 0, 16.5); and (0, 0, 19.5) magnetic modulations at 20K at the L_{III} (6.710 keV) resonance and confirmed the disappearance of these peaks on shifting off resonance in energy (that is, at: 20K and 6.725keV) and also by heating to above the Néel temperature while at the resonant photon energy (120K and 6.710keV).

Below 10K we looked for the (0.25, 0, 17.75) and (0.25, 0, 18.25) modulations (as expressed in a hexagonal basis) that would correspond to low temperature cubic site ordering but saw no evidence of extra intensity at these wavevectors.

We also observed, off resonance, (relatively) weak charge scattering peaks at the (0, 0, 6); (0, 0, 12); (0, 0, 15); (0, 0, 21) and (0, 0, 24) positions that would be expected to be forbidden for a straightforward ABABCBAC stacking with site equivalent form factors. We observed a temperature dependence of this scattering over a temperature range of 90K to 7K particularly in the case of the (0, 0, 24) reflection.

We had some indication that the small incident x-ray beam and the limited sample penetration allowed us to see one of the two mirror symmetries of the samarium structure preferred over the other. In a neutron experiment one would expect to see both forms occurring equally in a typical single crystal sample.

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Figure 1. The (0, 0, 16.5) L_{III} resonance and the strongly energy dependent fluorescent background.

Beam Time 16 – 24th July 1993.

Resonant Magnetic X-ray Scattering from UO₂

B.D. Gaulin (McMaster University), G.M. Watson (BNL), D. Gibbs (BNL), G.H. Lander (EITU, Germany)

We have used resonant magnetic X-ray scattering techniques at the MIV edge of uranium to study the magnetic properties of UO₂. These measurements were performed at beamline X22c of the NSLS.

Our measurements were made on a large single crystal of UO₂ which had been originally prepared with a well polished (110) surface. During the course of our measurements, we chose to mechanically roughen approximately 1/3 of the surface area. This allowed us to perform the resonant X-ray experiment on either the rough or smooth surface under identical conditions. Remarkably, we discovered a qualitative difference in the magnetic behavior near the phase transition in this material, as seen on the rough and smooth surfaces.

UO₂ undergoes a well-studied, strongly discontinuous phase transition from the paramagnetic state to a triple-Q, magnetically-ordered state at approximately 30.5 K. The behavior seen when the incident X-ray beam scatters from the smooth surface is characteristic of that expected from a system undergoing a discontinuous transition, and is shown in Fig. 1a). The order parameter drops precipitously to zero at T_N, and no fluctuations, as manifested in diffuse magnetic scattering, can be seen above T_N. Subsequent neutron scattering measurements on this same crystal show behavior similar to that reported previously; a sharp discontinuity in the order parameter and the presence of short range, non-divergent correlations above T_N. The behavior observed when the incident X-ray beam impinges on the rough surface is qualitatively different. Once again the order parameter falls discontinuously to zero at T_N. However, above T_N there is easily observable magnetic diffuse scattering which occurs for temperatures up to approximately 7 K above T_N. This scattering is anisotropic, with relatively short correlation lengths within the plane of the surface. These correlations are temperature dependent, and occur on a much longer length scale than the non-divergent correlations observed in the neutron scattering experiments. This behavior is shown for several temperatures above T_N in Fig. 1b), and should be contrasted with that seen on the smooth surface, Fig 1a)

These new X-ray measurements show the process of roughening the surface of this crystal induces the appearance of a second length scale in the fluctuations near the strongly discontinuous transition at T_N, and suggests that the origin of the sharp component lies in structural defects. Similar behavior has been observed in other magnetic systems.

Figure 1. Temperature dependence of scans taken along (111) through the (110) magnetic Bragg reflection from the polished surface (a) and the roughened surface (b). The critical temperature is 30.65 K

AN X-RAY MAGNETIC SCATTERING STUDY OF THE ANTIFERROMAGNETIC PHASE TRANSITION IN DYSPROSIUM METAL

G. Helgesen, J.P. Hill, T.R. Thurston, and Doon Gibbs (BNL)

The nature of the paramagnetic-to-helical magnetic phase transition in some rare earth metals (Tb, Dy, Ho) has been the subject of a large number of studies both experimentally by neutron scattering and theoretically by renormalization group techniques. Since the spatial resolution in x-ray magnetic scattering experiments is typically higher (~ 10 times) than in similar neutron scattering experiments, magnetic x-ray scattering can easily probe magnetic correlations over larger length scales than have been measured in earlier neutron experiments. X-ray resonant magnetic scattering studies of the helical phase of Ho have shown results which qualitatively agree with earlier neutron measurements, but they have also shown subtle changes in the magnetic correlation length below the Néel temperature T_N which had not been seen before. Dy has a magnetic structure similar to Ho and should show similar effects in x-ray magnetic measurements as those observed in Ho.

In order to study the magnetic scattering in Dy, the energy of the x-ray beam was tuned to the L_{III} absorption edge at 7.79 keV. The intensity of the resonant magnetic satellite peaks at $(0,0,2-\tau)$ and $(0,0,2+2\tau)$ was measured for temperatures between the ferromagnetic-to-helical transition at $T_C \sim 90$ K and $T_N \sim 181$ K. Here, τ is the wave vector of the spin helix along the hexagonal crystalline axis. The integrated intensity $I(\pi\tau)$ of the first order ($n=1$) and second order ($n=2$) magnetic satellite follows a power-law behavior $I(\pi\tau) \propto (T_N - T)^{\beta_n}$ in a temperature range of about 30 K below T_N . This is illustrated in Fig. 1. The fitted values of the exponents are $B_1 = 2\beta = 0.68 \pm 0.05$ and $B_2 = 1.70 \pm 0.10$. The value for the critical exponent $\beta = 0.34 \pm 0.03$ found in this experiment is slightly smaller than the value $\beta = 0.39 \pm 0.04$ found in earlier neutron experiments and smaller than $\beta = 0.42 \pm 0.04$ found by x-ray scattering in bulk Ho. However, the temperature dependence of the magnetic correlation length shows a behavior similar to that observed in x-ray experiments on Ho crystals, i.e., it is largest right below T_N and decreases at lower temperatures. This behavior may be related to magnetostriction effects in these rare earth elements.

AN X-RAY SCATTERING STUDY OF THE ANTIFERROMAGNETIC PHASE TRANSITION IN BULK AND THIN FILM CRYSTALS OF ERBIUM

G. Helgesen, J.P. Hill, T.R. Thurston, and Doon Gibbs (BNL), J. Borchers (NIST), C.P. Flynn and M.B. Salamon (U. of Illinois)

Metallic erbium has a second order phase transition to an antiferromagnetically ordered phase at a Néel temperature $T_N \approx 88$ K. In a temperature interval of about 30 K below T_N , the spins are ordered in a sinusoidally modulated structure with wave vector τ along the hexagonal c -axis of the crystal. Earlier x-ray scattering experiments have shown that the antiferromagnetic ordering of the spins also induces a modulation of the charge density, CDW, in the metal. The basic wave vector for this CDW is twice that of the magnetic wave vector, i.e., 2τ .

In order to study the magnetic scattering in Er, the energy of the incident beam was tuned to the L_{III} absorption edge ($E=8.36$ keV). The magnetic scattering at $(0,0,2+\tau)$ and $(0,0,2+3\tau)$ was then measured as a function of temperature. The intensity of the charge scattering at $(0,0,2+2\tau)$ and $(0,0,2+4\tau)$ was also measured. The intensity of the main magnetic satellite (at resonance) and that of the main CDW satellite are of the same order of magnitude ($\sim 10^4$ counts per second at 60 K) and they are about 200 times stronger than the higher order satellites, $(0,0,2+3\tau)$ and $(0,0,2+4\tau)$.

Our measurements showed that the integrated intensity, $I(n\tau)$, of the satellites at $(0,0,2+n\tau)$ where $n=1,2,3,4$ follows power-law behavior $I(n\tau) \propto t^{B_n}$ of the reduced temperature $t = (T_N - T)/T_N$ with exponents $B_1 = 2\beta = 0.96 \pm 0.06$ and $B_2 = 1.90 \pm 0.15$. Similar values for the exponents were also found for a 9500 Å thick Er film. These values are close to the values $B_n = 2n\beta$ with $\beta = 0.5$ found in systems which show mean field type of behavior. In these systems $[I(n\tau)]^{1/n}$ will fall on a single universal curve when the intensities are properly normalized. This is shown in Fig. 1 for a bulk Er sample. This result is quite surprising since Er was believed to belong to the 3-dimensional XY universality class with $\beta = 0.35$.

X-RAY RESONANT MAGNETIC SCATTERING FROM HOLMIUM FILMS

G. Helgesen, T.R. Thurston, J.P. Hill, and Doon Gibbs (BNL),
R.J. Kwo and M. Hong (AT&T, Bell Labs)

The magnetic properties of rare earth metals like Ho depend on a fine balance between exchange and crystal field interactions. It is known that elastic strain may change this balance. Since there is a mismatch between the lattice constant of bulk Ho and that of nonmagnetic Y used as a buffer layer in epitaxially grown Ho films, one may expect that the strain induced by this lattice mismatch may alter the magnetic properties. In order to investigate the possible effect of strain the magnetic scattering was measured as a function of temperature for a Ho film consisting of a sapphire substrate, an Y buffer layer, a 2 μm thick Ho(001) layer and a thin Y cap. Below the Néel temperature $T_N \approx 131$ K, Ho has a helical magnetic structure along the hexagonal crystalline axis with magnetic wave vector τ . In the experiment, the energy of the incident photons was tuned to the L_{III} absorption edge at 8.07 keV, and the intensity of the magnetic satellite peak at $(0,0,2-\tau)$ was measured in the temperature range from 10 K up to T_N . The integrated intensity, $I(\tau)$, found in the experiment could be fitted to a power-law $I(\tau) \propto (T_N - T)^{2\beta}$ for temperatures between 80 K and T_N as shown in Fig. 1(a). The value of the critical exponent β found in this experiment was $\beta = 0.42 \pm 0.05$ in good agreement with the value found in earlier experiments on bulk samples. Bulk samples of Ho also show a first order phase transition to a ferromagnetic cone structure below $T_C \approx 20$ K. However, no such phase transition was found in the Ho film for temperatures above 10 K.

The full width-at-half-maximum (FWHM) of the magnetic peak for scans along the $(0,0,L)$ direction in reciprocal space is shown in Fig. 1(b) and shows a clear dependence on the temperature. At and above the transition the peak is broadened due to critical scattering. The width of the peak is minimum right below the transition and there it is almost 40% smaller than the width of the $(0,0,2)$ Bragg peak. As the temperature decreases, the width increases as shown in Fig. 1(b). This change in the peak, width which is much larger than what has been seen in bulk Ho, may be attributed to epitaxial strain and magnetostriction effects.

J.P. Hill, G. Helgesen, G. Shirane and D. Gibbs (BNL)

Pure chromium forms a linearly polarized spin density wave (SDW) below $T_N=311\text{K}$. However in contrast to the majority of antiferromagnets studied to date with x-rays, it is an itinerant system. The SDW results from the combination of two helical SDWs of opposite helicity which pair electron states $(k, \uparrow)$ and $(k \pm Q, \downarrow)$. The SDW is stable when these states exist on the respective Fermi surfaces and Q is then the wave vector which "nests" the electron and hole Fermi surfaces. For $120\text{K} < T < 311\text{K}$ the spins are perpendicular to the modulation wave-vector, Q (transverse phase). Below $T_{SF} = 120\text{K}$ the spins flip and lie along Q (longitudinal phase).

We have observed the SDW in Cr for the first time with x-rays. Fig. 1 shows the peak intensity of the $(2-Q, 0, 0)$ magnetic peak as a function of temperature. At $T_{SF} = 120\text{K}$, the spins flop into the longitudinal phase. This puts them in the diffraction plane, reducing the cross-section by $\sin^2\theta$ and the signal becomes unobservable. The count rate of 10cps at X22C represents non-resonant magnetic scattering from an average moment of $0.62\mu_B$ per atom.

Accompanying the SDW is a second harmonic charge density wave (CDW) induced through electron-phonon interactions which in turn generates a strain wave that is readily observable with x-rays as diffraction peaks at $(n \pm 2Q, 0, 0)$. Fig. 2 shows a scan along $(H, 0, 0)$. The intensity of the second harmonic corresponds to a distortion amplitude of 0.1% of the lattice constant. In fact the SDW is not a pure sine wave, and we have been able to observe for the first time the "squaring" of the CDW, with the observation of peaks at $(n \pm 4Q, 0, 0)$, as shown in Fig. 2. The peaks are too large to be diffraction harmonics of a pure sine wave and represent a 2nd harmonic of the CDW which is 2% of the first. We have investigated the temperature dependences of these harmonics and find them to obey mean field scaling.

Fig. 1

Fig. 2

DYNAMIC SCALING OF FRACTALLY ROUGH SURFACES

J. Krim and G. Palasantzas (Northeastern University), C. Thompson (Polytechnic University), Y.P. Feng and S.K. Sinha (EXXON)

We carried out x-ray reflectivity measurements in order to determine the dynamic scaling properties of silver films deposited onto silicon substrates which were held at liquid nitrogen temperatures. By measuring x-ray reflectivity at the specular condition, and measuring the diffuse scattering, the evolution of the surface roughness was monitored as a function of film thickness for a sequence of seven film thicknesses. Our chamber allowed the x-ray scattering to be performed under UHV conditions with the substrate continually at low temperature. After the entire deposition series was completed, with approximately 1000 Angstroms of silver on the substrate, we permitted the sample to warm to room temperature under vacuum and re-measured the reflectivity. We note dramatic changes in the reflectivity upon warm-up, as seen in the figure, which we attribute to collapse of structures throughout the film. Note that in the figure, the reflectivity for the warmed sample has been shifted for clarity. The fragility of the structure of the low temperature deposition is consistent with previous observations from adsorption isotherms [1]. We also confirmed earlier measurements [2] on the dynamic scaling of silver deposited on room temperature silicon, and the results were consistent with those previously obtained.

[1] V. Panella and J. Krim, submitted to Phys. Rev. E.

[2] C. Thompson, G. Palasantzas, Y.P. Feng, S.K. Sinha, and J. Krim, submitted to Phys. Rev. B.

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RESONANT MAGNETIC SCATTERING OF NpAs : OBSERVATION OF CRITICAL FLUCTUATIONS

X22C

S. Langridge, W. G. Stirling (Keele U, UK), G. H. Lander, J. Rebizant, and J. C. Spirlet (EITU, Karlsruhe, Germany) and D. Gibbs (Physics, BNL)

The previous experiments on NpAs (see report of exp. 3/12-3/21/92) were extended at the resonance energy (3.852 keV) and essentially completed. Extensive studies of the magnetic structure were made. An usual 'domain reorientation' effect was observed just prior to a 1st-order phase transition between two magnetic phases. The domain orientation meant that almost a single domain was formed in the near surface region. This observation explained many of the earlier puzzles. Such effects are not observed in neutron scattering because the latter is a bulk probe. High resolution experiments to examine the lattice were performed at 8 keV with a Ge(111) analyzer.

Our attention then focused on the region near T_N in which critical fluctuations were observed qualitatively in our earlier experiment. In this run we obtained excellent data sets — see the figure — and are now in the process of extracting quantitative parameters for the critical fluctuations.

From such scans we can extract (after deconvolution with the instrumental resolution) the real space correlation widths ζ and their amplitudes as a function of T . These appear to be far longer in real space than observed at similar reduced temperatures with neutron scattering. This situation is similar to the effects observed by Thurston and Gibbs and collaborators on holmium. It shows that studies of critical magnetic scattering with the X-rays are of considerable interest.

Beam time : 23 Nov. - 3 Dec. 92

EXAMINATION OF THE CHARGE DENSITY WAVE IN ALPHA-URANIUM UNDER UNIAXIAL STRESS

X22C

J. C. Marmeggi (CNRS and Univ. of Grenoble), G. H. Lander (EITU, Karlsruhe, Germany) P. Gehring and D. Gibbs (Physics, BNL)

The object of the present experiments was to study the development and pressure-dependence of the charge-density wave (CDW) in α -U under the application of uniaxial stress. The main innovation in the experiment was the design and fabrication (at the CNRS, Grenoble) of a special rig in which uniaxial stress could be applied to a single crystal. The rig was sufficiently small to fit inside the dispex of X22C. The main success of this experiment was in the testing of the pressure rig to give uniaxial stress up to 0.8 kbar. We acknowledge the help of the technical staff in the Physics Department for much help in setting up this apparatus, especially Al Roberts and Bill Schoenes.

Our experiments were conducted on the same sample used for earlier uniaxial-stress experiments at the ILL, Grenoble with neutrons [1]. We discovered, however, that the mosaic of the near-surface region of this crystal had been severely damaged by stress applied in the previous experiments. The mosaic of the bulk, as measured in neutron experiments, was still reasonable, but the near-surface region, as examined by X-rays, was essentially useless for high-resolution synchrotron experiments. This problem was somewhat ameliorated by electro-polishing, but in the end prevented a truly quantitative experiment from being performed. A new crystal is being prepared and we hope to continue these experiments. Earlier experiments on X22C gave important information on the CDW at ambient pressure [2].

Our best data was obtained on the so-called 'Smith' satellites [3]. Surprisingly, these were found to decrease with uniaxial stress applied in the $[011]^*$ direction, which was not the case for the neutron experiments [1]. This, too, may be related to the near-surface behavior. We were able to observe 'critical effects' (i.e. the peaks wider than the resolution function) in the 'Smith' satellites near T_C for the CDW, and the behavior appears consistent with the recent ideas of Yamada [4]. A more thorough examination of this is a realistic goal in the next experiment, as well as a study of the CDW satellites.

JCM thanks the "Ministère des Affaires Etrangères" and the University of Grenoble for travel support. GHL thanks BNL for support.

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[3] Smith et al., Phys. Rev. Letts **44**, 1612 (1980) [4] Yamada, Phys. Rev. (in press)

Beam time : 11-18 June 1992

RESONANT ENHANCED MAGNETIC X-RAY SCATTERING FROM $USb_{0.8}Te_{0.2}$.

W.J.Nuttall, W.G. Stirling (Keele U. U.K.), G.H. Lander (EITU, Karlsruhe, Germany) and Doon Gibbs (Physics, BNL).

We have observed critical behavior in the incommensurate anti-ferromagnet $USb_{0.8}Te_{0.2}$ in the vicinity of the Néel temperature ($\sim 207K$). Our measurements are obtained from a single crystal sample (mosaic $\sim 0.06^\circ$ FWHM), utilizing the resonant enhancement available at the M_{IV} edge.

The use of synchrotron x-ray scattering to study critical phenomena in lanthanide and actinide systems is particularly powerful given the extremely high q-resolution possible compared with neutron techniques. Several x-ray experiments have, as a result of this resolution, observed novel and previously unexpected two-component lineshapes including long-ranged anti-ferromagnetic (AF) order. This is postulated to relate to the near-surface nature of the x-ray probe.

Figure 1.

Our X-ray studies complement neutron studies performed at Riso National Laboratory, Denmark. In that case the AF phase below T_N was observed to order on a length scale equivalent to the neutron resolution of ~ 0.015 RLU (FWHM).

As is shown in Fig. 1., however, our x-ray results reveal that the AF phase in $USb_{0.8}Te_{0.2}$ has remarkably limited long-range order, nor do we see any evidence of a two component lineshape.

As Fig. 1. illustrates, the observation of resolution limited order in the neutron scattering experiment was simply coincidentally the actual limit of the ordered length scale in the sample. A detailed analysis of both the neutron and x-ray experiments will be undertaken in the near future. Only such an analysis will show whether a two component lineshape is needed to describe the x-ray data.

In addition to our critical scattering data we performed a high-resolution experiment to look at the lattice distortions accompanying the Néel and Curie transitions in this system.

Beam Time: 9 - 16th July 1993.

X-RAY MAGNETIC SCATTERING FROM SAMARIUM

S. Shaikh, E.M. Forgan (Birmingham, U.K.), M.M.R. Costa (Coimbra, Portugal), M.J. Cooper (Warwick, U.K.), S. Langridge, W.G. Stirling (Keele, U.K.) and D. Gibbs (BNL)

This experiment was in continuation of x-ray magnetic diffraction measurements at Daresbury, on single-crystal **Samarium**, in which resonant enhancement at L_{II} and L_{III} absorption edges was studied. The energy-dependent absorption was measured on X22C using a $5\mu m$ Sm foil, at both L_{II} (Fig. 1) and L_{III} edges. Studies of the energy-dependence of the $(0,0,7.5)$ magnetic satellite were made with a Ge analyser crystal to reduce the effect of the strong Sm fluorescence. Some unexplained difficulties were encountered with the reproducibility of the x-ray energy. A typical example of a $\theta/2\theta$ scan at 20K is presented in Fig. 2. An interesting increased q-width was observed off-resonance; this will be followed up in future experiments. Polarisation analysis at the L_{III} edge was attempted using a Cu (220) analyser crystal, chosen to give $\sim 90^\circ$ scattering at the appropriate energy. Although this crystal had a good mosaic spread and a reasonable reflectivity, the magnetic signal was found to be too weak to study quantitatively in either the in-plane or out-of-plane configurations. Work on improved polarisers will continue with the intention of continuing with these investigations. Nevertheless, it is hoped to perform a second set of measurements at X22C, with a solid-state detector, to investigate the temperature dependence of the hexagonal-site ordering, the cubic-site ordering at 13K, the satellite q-widths, and the $2q$ lattice distortion satellites.

Fig. 1 Absorption coefficient the L_{II} edge

Fig. 2 Magnetic satellite reflection at the L_{III} edge energy.

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Magnetic critical scattering in UAs.
C. Vettier, F.de Bergevin, P.Dalmas, G. Helgesen, D.L. Gibbs, J.B.Hastings

We have studied the onset of magnetic ordering in UAs by using resonant magnetic x-ray Bragg scattering. UAs has the simple NaCl crystal structure and is known to order antiferromagnetically below $T_N = 123$ K as a type I antiferromagnet (propagation vector [001] or X point in the Brillouin zone) with the magnetic moments along the cubic axis of the crystal structure. This phase transition is known to be weakly first-order. However, neutron scattering experiments have revealed the existence of magnetic critical scattering above T_N at incommensurate positions [00 ζ] in reciprocal space. This scattering disappears below T_N when the commensurate long range order sets in. The purpose of our experiments was twofold: an investigation of the correlation lengths near T_N and a study of the surface effects. We have taken advantage of the resonant enhancement of the magnetic x-ray scattering cross section by tuning the x-ray energy at the uranium M_{IV} absorption edge. At this energy, absorption becomes very important and x-ray are probing the top 2000 Å layer near the crystal surface. Preliminary results have revealed new features in the phase transition. First, the observed ordering temperature is lower (≈ 116.4 K) than previously reported values, which could be attributed to stoichiometry or near-surface effects. Second, as shown in the figures, two temperature regimes can be distinguished. Above $T_N + 1$ K, the magnetic critical scattering is clearly peaked at incommensurate positions and extends towards the commensurate position. Closer to T_N , some diffuse scattering develops at the X point before long range order develops. This does not correspond to the results on bulk samples with neutron scattering. The origin of this scattering has to be investigated. Further work will involve a careful study of the lineshapes of both components as function of temperature.

Figures: Longitudinal scans in UAs across the incommensurate and commensurate positions at various temperatures.

The Interaction of Steps and Surface Reconstructions on Stepped Pt(001)

G. M. Watson (BNL), D. Gibbs (BNL), M. Yoon (MIT), S. G. J. Mochrie (MIT), and D. M. Zehner (ORNL)

We have used X-ray scattering to study the morphology and surface reconstructions of a vicinal Pt(001) surface between 300 and 1850 K. Our sample was miscut by 1.4° from the (001) direction towards the (110) direction. Below 1620 K, we find that the surface facets to form step-free domains and domains with an ordered distribution of steps. The step-free facets are hexagonally reconstructed and show a phase behavior similar to that of the Pt(001) surface [1]. The terraces of the stepped domains are reconstructed to form a buckled and rotated hexagonal structure. Surface buckling refers to the sinusoidal displacement of atoms along the surface normal, and is a characteristic of the hexagonal reconstructions of Pt and Au (001) surfaces [1]. Consistent with the ideas of Grey and Bohr [2], it is remarkable that the step edges are not aligned with a high-symmetry direction of either the hexagonal overlayer or the underlying bulk lattice, rather they are aligned with the buckling wavevector.

These results are illustrated in Fig. 1 which show scans taken along the direction of the buckling wavevector. The peaks at $H = 1.00$ and 1.22 a^* correspond to the $(H,K)=(1,1)$ bulk truncation rod and the principal hexagonal surface rod from the (001)-facets. The peaks at $H=0.98$ and 1.03 a^* are truncation rods from the stepped domains and pass through the (111) and $(1\bar{1}\bar{1})$ bulk Bragg reflections respectively. They are separated by the step wavevector δ_s . δ_s is inversely proportional to the average terrace width and its direction is perpendicular to the steps. The peak at $H=1.23$ a^* corresponds to the principal hexagonal wavevector of the reconstructed tilted phase. The difference between this hexagonal rod and the (111) truncation rod corresponds to the buckling wavevector, δ . It is clear that the step wavevector is parallel to the buckling wavevector on the stepped domains. As the temperature is lowered, additional harmonics of the step wavevector appear and grow. At 1500 K, the step wavevector is precisely $1/4$ the buckling wavevector. Thus, there is an incommensurate-commensurate transformation.

Figure 1. Scans along the solid line shown in the inset for temperatures from 1281 to 1619 K. The inset shows a map of the H-K plane of reciprocal space for $L=0.05$ c^* at a temperature of 1619 K.

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Effects of Composition and Strain on Bonding in Ge-Si Alloys

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Silicon and germanium form a continuous solid solution over their entire alloy composition range. Natural Si-Si and Ge-Ge bonds differ in length by approximately 4%. When Si and Ge are alloyed the strain caused by the differing bond lengths raises the crystal energy above that of Pure Si or Pure Ge. Theoretical studies have predicted that the Ge-Ge, Ge-Si, and Si-Si bonds in relaxed bulk alloys will maintain three distinctly different lengths which vary linearly with composition.

In this study we used relaxed MBE deposited single crystalline alloy films grown on clean Si(100) substrates. Alloy layer thicknesses greater than the critical thicknesses were used. Rutherford Back Scattering (RBS) was used to determine the composition and thickness of the alloy films. X-Ray Diffraction (XRD) was used to measure the degree of uniaxial expansion (residual strain) in the alloys. The Ge-Ge and Ge-Si bond lengths were determined from Ge K-edge EXAFS collected using an electron yield detector in a low angle configuration on beamline X23A2 of the National Synchrotron Light Source at Brookhaven National Laboratory.

The measured $\text{Ge}_x\text{Si}_{1-x}(400)$ plane spacing was compared with the lattice spacing predicted by Vegard's Law and the percent lattice expansion is plotted in Figure 1. The bond lengths determined by EXAFS are also plotted in Figure 1. To compare the measured bond lengths with those of bulk Ge-Si alloys it is necessary to correct for the bond compression caused by the residual biaxial compression in the films. Measurement of the $\text{Ge}_x\text{Si}_{1-x}(022)$ plane spacing provides the information necessary to make a simple geometrical correction to the measured bond lengths. Preliminary $\text{Ge}_x\text{Si}_{1-x}(022)$ XRD data indicates that the variation of bond length with composition, indicated by the EXAFS measurements, may be caused, in part, by the change in strain. Experiments to determine the effects of residual strain on atomic bonding in Ge-Si alloys are in progress.

FIGURE 1. 1) Measured Ge-Ge and Ge-Si bond lengths. 2) Bond lengths geometrically corrected for the distortion of the unit cell as measured by XRD. 3) Uniaxial lattice distortion as measured by XRD.

THE ELECTRONIC PROPERTIES OF CERIUM IN $\text{CeFe}_4\text{P}_{12}$

Mark R. Antonio, J. Simon Xue, Wesley T. White, L. Soderholm, (Argonne National Laboratory), Farrel W. Lytle (EXAFS Co.), and Susan M. Kauzlarich (U.C. Davis)

Rare earth-transition metal phosphides with the composition $\text{RE}M_4\text{P}_{12}$ ($\text{RE} \equiv \text{La-Eu}$, $M \equiv \text{Fe, Ru, Os}$) crystallize with the skutterudite type structure of $\text{LaFe}_4\text{P}_{12}$. The unit cell volume of $\text{CeFe}_4\text{P}_{12}$ suggests that cerium may be intermediate or mixed valent. By use of L-edge XAFS, we have determined the f-element valence distribution in $\text{REFe}_4\text{P}_{12}$ for $\text{RE} \equiv \text{La, Ce, and Pr}$. Electron-yield XAFS were collected at ambient conditions for black crystalline powders of $\text{REFe}_4\text{P}_{12}$ at the RE L3- and L1-edges on beam line X-23A2 with a Si<311> double crystal monochromator. Whereas the formal oxidation states of La in $\text{LaFe}_4\text{P}_{12}$ and Pr in $\text{PrFe}_4\text{P}_{12}$ are trivalent, the Ce XANES for $\text{CeFe}_4\text{P}_{12}$ is complex, indicating that although cerium is primarily trivalent, there is evidence of complex electronic behavior in $\text{CeFe}_4\text{P}_{12}$ (see Figure).

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THE OXIDATION STATE OF CERIUM IN Ce_2MoO_6

Mark R. Antonio, J. Simon Xue, L. Soderholm, (Argonne National Laboratory), and Farrel W. Lytle (EXAFS Co.)

As part of our studies of binary cerium sesquioxides ($\text{Ce}_2\text{O}_3 \cdot n\text{MO}_3$ for $n = 1, 2, 3$ and $M \equiv \text{Mo, Te, W, U}$), we have investigated the chemical state of cerium in Ce_2MoO_6 through Ce L-edge XAFS. L_3 - and L_1 -edge electron-yield XAFS were collected at ambient temperature on beam line X-23A2 with a Si<311> double crystal monochromator. The normalized Ce L-edge XANES of Ce_2MoO_6 and CeO_2 are displayed in the Figure. The intense single resonance at 5722.2 eV in the L_3 -edge XANES of Ce_2MoO_6 is typical of trivalent cerium. The position (6563.6 eV) of the L_1 -edge peak of Ce_2MoO_6 with respect to that of ca. 6562 eV for Ce^{III} compounds and ca. 6574 eV for Ce^{IV} compounds confirms the presence of Ce^{III} cations in Ce_2MoO_6 . These Ce L-edge XAFS measurements reveal that Ce_2MoO_6 does not contain a mixed-valence distribution of trivalent and quadrivalent cerium, i.e., $\text{Ce}^{\text{III}}\text{Ce}^{\text{IV}}\text{Mo}^{\text{V}}\text{O}_6$. Rather, to the level of sensitivity of the technique, the oxidation state of Ce is trivalent.

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TEMPERATURE EFFECT OF BACTERIAL PHOTOSYNTHETIC REACTION CENTER STRUCTURE PROBED BY FE SITE EXAFS SPECTRA

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The bacterial photosynthetic reaction centers (RC) are the devices for the primary photoinduced charge separation in photosynthesis. A pair of chlorophylls in RC acts as a primary electron donor which triggered a series of electron transfer processes. Followed by subsequent electron transfer from the special pair chlorophyll to other chromophores in the RC, the charge separation across the membrane was eventually achieved. The Fe site of the RC (Fig. 1) is on the electron transfer path and at the vicinity of the two quinones involved in the electron transfer. The study of kinetics for electron transfer has revealed temperature dependence of the electron transfer rate. The electron transfer from the special pair chlorophyll to the bacterial pheophytin (H_A) is 1.2 ps at 10K, and 3 ps at room temperature. Despite many experimental and theoretical studies that have been done in this field, the precise temperature dependence of the RC protein global structure or the electron donor to acceptor distances remains questionable.

An EXAFS study was conducted on X23A2 to investigate the temperature effect on the RC structure using the Fe site as a probe. The EXAFS scans were collected at room temperature and at 20K. Preliminary results have indicated certain structural differences of RC at these two temperatures (Fig. 2). Although, the EXAFS technique can only probe the local structure around the Fe and can not conclude any global structural change in the RC protein as the temperature changes, the difference of EXAFS spectra around the Fe site at these two temperatures has indicated (1) a strong evidence of the temperature dependence of the RC structure; (2) a potential correlation between the structure around the Fe site and the reaction rate of the electron transfer in RC. Further data analysis will reveal the origin of the observed structural difference and will lead to a better understanding of photosynthesis in nature.

Figure 1. Structure of bacterial photosynthetic reaction center (RC) chromophores.

Figure 2. EXAFS spectra of RC (R26 sphaeroides) in PVA film at different temperatures.

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COMPARATIVE STRUCTURAL STUDIES OF CO/CU MULTILAYERS

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The interfacial structure in Co/Cu multilayers is an important parameter for understanding the magnetic properties of this system. Unfortunately, measurement of this structure is quite difficult. X-ray diffraction data are insensitive to compositional modulation and the satellite structure is caused by lattice spacing modulation. The simultaneous presence of different crystal structures and/or gradual structural transitions with varying layer thicknesses complicate the interpretation of satellite behavior. NMR measurements provide an alternate structural probe and the results from several studies produce an intriguing blend of similarities and inconsistencies. Le Dang, et al. [1] studied Co/Cu samples prepared by MBE and reported (i) abrupt interfaces, (ii) Co layers that were dominantly FCC in structure with about 20% of the Co's located in an HCP environment and (iii) an inplane expansion for the Co layers. The NMR data indicated a 0.3% expansion while earlier X-ray data gave an expansion $\geq 1\%$ [2]. In a recent study, other MBE samples gave a pure FCC stacking with atomically flat interfaces [3]. Mény, et al. [4] investigated sputtered Co/Cu samples. They reported sharp interfaces occurred if no defects were present in the Co layers but the presence of defects broadened the interface to 3 monolayers. They found no significant HCP Co for Co layers up to 15Å in thickness. de Gronckel, et al [5,6] studied Co/Cu prepared by e-beam evaporation. They found (i) a FCC structure for the Co layers up to 20Å in thickness, (ii) stacking faults developed for layer thicknesses above 20Å and (iii) inplane strain that was function of both the Co and Cu layer thicknesses.

We are just beginning EXAFS studies of Co/Cu multilayers. Our intent is to compare EXAFS data for samples of comparable layer thicknesses prepared by MBE and by sputtering. Limited data and analysis complications arising from the presence of substrate glitches prevent us from reporting structural results at this time. We simply note that the signal to noise ratio for data taken at room temperature is adequate to track the oscillations out to at least $12\text{\AA}^{-1}$ in momentum space. This range was adequate to identify both systematic trends in the first shell surrounding Co and the presence of higher shells in Co/Ag multilayers [7].

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EXAFS STUDIES OF MECHANICALLY DEFORMED POWDERS OF IMMISCIBLE ELEMENTS

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We have performed extended X-ray absorption fine structure (EXAFS) measurements on mechanically deformed powders of $\text{Cu}_{70}\text{Fe}_{30}$ and $\text{Ag}_{70}\text{Fe}_{30}$ in an attempt to gain insight into the alloying behavior of elements which do not 'mix' under equilibrium conditions. The mechanical deformation of the powders took the form of 20 to 200 hours of continuous ball-milling in an atmosphere of argon gas. X-ray θ - 2θ diffraction patterns obtained after 20 hours of ball-milling illustrate, for Cu-Fe, a single set of fcc diffraction peaks with no signs of a second phase. Alternatively, for Ag-Fe, the X-ray diffraction pattern showed a single set of fcc diffraction peaks but some peaks displayed visible asymmetries at d-spacings corresponding with previous bcc-Fe diffraction features suggesting that the Fe had not fully mixed with the Ag. Ball-milling of the Ag-Fe powder for upwards of 200 hours was effective in eliminating these peak asymmetries leading one to believe that alloying had occurred.

X-ray absorption spectra were collected for the K absorption edges of Cu, Ag, and Fe using the NIST X23A2 beamline. Following established EXAFS analysis procedures the extended fine structure appearing above the absorption edge was isolated, normalized to the edge step and energy, and converted to photoelectron wave vector (k) space. A non-oscillatory background curvature was removed in k -space by fitting to a cubic spline curve. These data were then Fourier transformed to a radial coordinate. Figure 1 (a) is a plot of Fourier transformed Cu and Fe EXAFS data for the $\text{Cu}_{70}\text{Fe}_{30}$ powder sample ball-milled for a period of 20 hours; panel (b) are Fourier transformed Ag and Fe EXAFS data for the $\text{Ag}_{70}\text{Fe}_{30}$ powder ball-milled for a period of 200 hours. Data from standards of bcc Fe and fcc Ag are presented in panels (a) and (b), respectively, for comparison purposes. The inset graphic to panel (a) is a schematic of the fcc unit cell indicating how the lattice sites correspond with the Fourier features.

In Figure 1(a) it is clear that the Fourier transformed Fe and Cu data are qualitatively very similar. Fourier peaks corresponding with the first four neighbors of the fcc unit cell appear in both data sets at approximately the same radial distances and having the same relative amplitudes. In comparing the Fe data to the bcc standard there is no sign of a bcc component in the Fe transform. Thus, we conclude that in the case of $\text{Cu}_{70}\text{Fe}_{30}$ 20 hours of

ball milling is effective in mixing the Cu and Fe even at the atomic level. First shell modeling of these data using FEFF v.3.11 indicate the local chemistry around both constituents is close to the stoichiometric ratios.

Alternatively, the Fourier transformed Fe and Ag data presented in panel (b) illustrate that the Fe remains in the bcc structure and Ag in the fcc structure. This is most clearly seen in comparing the Fe data to the bcc standard and the Ag data to the Ag standard. First shell modeling of these data indicate little or no mixing has occurred in the short range structure.

These results indicate that X-ray diffraction used alone is insufficient in determining the degree of alloying in nanostructured materials. For example, in the X-ray diffraction pattern of the AgFe powder milled for 200 hours there is no indication that Fe remained in a bcc phase, however, the EXAFS results presented here show unambiguously that Fe remains both chemically and structural separated from the Ag even after 200 hours of ball-milling.

Figure 1. Fourier transformed EXAFS data for (a) $\text{Cu}_{70}\text{Fe}_{30}$ powder ball-milled 20 hours, and (b) $\text{Ag}_{70}\text{Fe}_{30}$ powder ball-milled 200 hours. The data have been prepared using a k -range of $2.3\text{--}14\text{\AA}^{-1}$ and a k^2 weighting.

X23A2

Glancing Angle EXAFS Studies of Copper "Pre-melting" at the Cu/Al₂O₃ Interface

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A number of experiments over the last few years have shown that surfaces play an important role in melting. Premelting near internal interfaces, however, have not been nearly as well studied. These concepts are important not only for understanding basic melting process, but also in technologies such as power metallurgy, crystal growth, and advanced composite materials. XAFS with glancing-angle x-ray reflectivity is performed to study the "pre-melting" behavior of Cu at buried interfaces in Cu/Al₂O₃ and other systems. The sample was fabricated by thermally evaporating 1000 Å Cu on 1 square inch quartz substrate inside an evacuated belljar at 10⁻⁶ torr. The sample was then quickly transferred to another vacuum chamber where ~700 Å of Al₂O₃ was e-beam evaporated over the Cu film. The goal of this experiment is to study the magnitude and anisotropy of vibrational amplitudes as a function of temperature below the melting point. XAFS and reflectivity measurement were done with x-ray polarization parallel and perpendicular to interface at various temperature. By varying the angle of incidence, it is possible to obtain depth-dependent structural information with depth varying from 10 Å to 50 Å. From these experiments the effect of the top several layers near the interface is expected. Earlier results implied large in-plane anharmonic motion in the top few layers. Here, we are repeating the measurements with higher-quality samples and more sophisticated analysis. Data analysis of both the reflectivity and XAFS on these measurement is currently underway.

Fig.1 X-ray reflectivity measured at room temperature, 9.3 Kev, and having ϵ parallel to the interface.

X23A2

IN-SITU XAS OF CARBON SUPPORTED Pt ALLOY ELECTROCATALYSTS

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Alloying of carbon supported Pt catalysts with first row transition metal elements enhances the electrocatalysis of oxygen reduction in fuel cells. All the first row elements enhance the catalysis, with Cr and Mn yielding the greatest effects. *In situ* XAS studies were made in an electrochemical cell in 1 M HClO₄ at the respective transition metal K-edges and at the Pt L₂ and L₃ edges. This permitted calculation of the effect of the alloying element on the Pt-Pt bond length and on the Pt d-band orbital vacancy (Du). The results are summarized in Table 1. The Pt-Pt bond length is correlated with Du. At 0.3 V, where there is no adsorption on Pt, changes in Du are due to the alloying metal. Any changes in Du that occur on going to 0.6 V are due to adsorption of O species on Pt. There is a large change in Du for the unalloyed catalyst, indicating adsorption of O species from the electrolyte. The alloying elements inhibit this adsorption, thus increasing the available bare Pt sites for O₂ adsorption, hence the enhanced catalysis for O₂ reduction.

Table 1. TWO SHELL FITS FOR Pt EXAFS OF ALLOY CATALYSTS, 0.3 V SCE:
ALSO THE Pt d-BAND ORBITAL VACANCY AT 0.3 V AND 0.6 V SCE

SHELL	DATA	ALLOYING ELEMENT (M)				
		Mn	Cr	Fe	Co	Ni
Pt-Pt	N	7.8	11.1	6.5	6.9	9.1
	R (Å)	2.76	2.71	2.70	2.68	2.68
	$\Delta\sigma^2$ (Å ²)	0.006	0.006	0.004	0.006	0.007
	ΔE_0	1.2	4.8	2.1	5.7	7.5
Pt-M	N	2.75	2.07	3.3	2.48	2.72
	R (Å)	2.68	2.70	2.64	2.63	2.61
	$\Delta\sigma^2$ (Å ²)	0.002	0.004	0.005	0.006	0.011
	ΔE_0	-8.0	-7.4	-5.6	-8.4	-9.1
Du, 0.3 V SCE		0.331	0.336	0.368	0.401	0.409
Du, 0.6 V SCE		0.344	0.358	0.370	0.390	0.404

N = Coordination number, R = Bond length, $\Delta\sigma^2$ = Debye-Waller factor

ΔE_0 = Energy shift

Du for Pt foil = 0.3 (Orbital vacancies per Pt atom)

Du for carbon supported Pt; 0.329 at 0.3 V SCE, 0.370 at 0.6 V SCE

R (Pt-Pt) = 2.77 Å for Pt foil and carbon supported Pt

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IN-SITU XAS STUDIES OF CHEMICALLY-MODIFIED MnO_2 ELECTRODES

J. McBreen (BNL), D. Qu and B. E. Conway (Univ. of Ottawa)

Manganese dioxide (MnO_2), the active material in commercial alkaline batteries, cannot be recharged. The addition of small amounts of Bi render it rechargeable. The mechanism is not understood. *In situ* XAS measurements were done in an electrochemical cell with a 9 M KOH electrolyte. Spectra were obtained at the Bi L_3 edge in transmission and at the Mn K-edge in the fluorescence mode. Spectra were recorded at several potentials during charge and discharge. The Bi XANES showed reduction to Bi metal on deep discharge. On charge the Bi is oxidized prior to the onset of oxidation of the manganese active material. In partially charged and fully charged electrodes the Bi is Bi (III) but is not Bi_2O_3 (see Fig. 1). Table 1 shows that the first peak of the Fourier transform for the Bi EXAFS could be fitted to a two shell fit, indicating a distorted octahedral coordination. Figure 2 shows that the Mn EXAFS of the recharged electrode were identical to that for the undischarged electrode. These results elegantly confirm the reversibility of the system, particularly with respect to structure changes.

Table 1. Parameters for the two Bi-O shells

Electrode	N	R	Calculated Parameters	
			$\Delta\sigma^2(\text{\AA}^2)$	$\Delta E_0(\text{eV})$
Charged	4.0	2.19	-0.0026	1.68
	2.0	2.31	-0.006	18.9
Recharged	4.0	2.16	-0.001	2.24
	2.0	2.29	-0.005	18.3

Fig. 1 RDF for Bi in charged MnO_2 (—), and Bi_2O_3 (---).

Fig. 2. Mn RDF before discharge (—), and after recharge (---).

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XAS STUDIES OF CLUSTERS AND COMPLEXES IN POLYMER ELECTROLYTES

J. McBreen, X. Q. Yang and H. S. Lee (BNL)

Poly (ethylene oxide) (PEO)/salt complexes are an important new class of electrolytes. Their conductivity depends on ion mobility in the polymer and on ion pairing and coulombic interactions among ionic carriers. Only the amorphous phases in the polymer are conductive. In the present work EXAFS was used to determine the structure of $\text{NiBr}_2(\text{PEO})_8$ and the mixed salt/PEO complexes of $\text{ZnBr}_2/\text{LiBr}(\text{PEO})_{12}$ and $\text{ZnBr}_2/\text{CaBr}_2(\text{PEO})_{12}$ in the temperature range of 25°C to 120°C. Figure 1 shows a comparison of the Fourier transforms of the Zn EXAFS for $\text{ZnBr}_2(\text{PEO})_8$ and $[0.33\text{ZnBr}_2 + 0.67\text{CaBr}_2](\text{PEO})_{12}$ at 80°C. In the $\text{ZnBr}_2(\text{PEO})_8$ at 80°C each Zn was coordinated with 1.68 Br atoms at a distance of 2.43 Å and 4.34 O atoms at a distance of 2.21 Å. In all of the mixed salt complexes at 80°C the Zn was coordinated with 4 Br atoms at a distance of 2.42 Å. There was no coordination with O. The results indicate the formation of ZnBr_4^{2-} complexes. The CaBr_2 acts as a Br^- ion donor.

Figure 2 shows a comparison of Fourier transforms for $\text{NiBr}_2(\text{PEO})_8$ at 25°C and 120°C. Ni is coordinated with both O and Br atoms. On increasing the temperature the O coordination decreases and the Br coordination increases, indicating the formation of NiBr_2 salt clusters in the polymer.

Fig. 1. RDF for $\text{ZnBr}_2(\text{PEO})_8$ (---) and $[0.33\text{ZnBr}_2 + 0.67\text{CaBr}_2](\text{PEO})_8$ (—).

Fig. 2. RDF for $\text{NiBr}_2(\text{PEO})_8$ at 25°C (—) and 120°C (---).

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X23A2

X-RAY ABSORPTION STUDIES OF Ba ENVIRONMENTS IN BaO-Ga₂O₃-GeO₂ GLASSES

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Conclusions from Ge and Ga EXAFS for Ba-gallogermanate glasses [1] indicate that Ge or Ga coordination changes cannot be the structural cause behind the physical property variations and the so-called "germanium anomaly", where properties of these glasses have a maximum (or minimum), as alkali content is varied. To see if the structural mechanisms may be observed in the network modifying Ba environments, initial Ba L₁ edge X-ray absorption spectra were gathered to investigate the Ba environments in the glasses and the crystalline models: BaGa₂Ge₂O₈ (BGG-An) [2] and BaCO₃. Partial RDFs indicate interesting differences between the glasses and BGG-An, as shown in Figure 1. As expected, most atomic shells surrounding Ba in the glasses are damped versions of corresponding shells for the model. However, the second shell for BGG-An (near 3.0 Å) corresponds to a split shell for the glasses. This split second shell may be due to shifting of the two similar Ba-(Ga,Ge) distances in BGG-An to longer and shorter distances in the glass, and may indicate differences in the tetrahedral network in the glass compared with BGG-An.

Fig.1. Ba partial RDF for the standard BGG-An (see text) and glass I-40 .

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X23A2

EXAFS study Er doped Tellurite glasses.

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Extended X-ray Absorption Fine Structure measurements were performed at the Er L₃ edge on erbium doped tellurite glasses. Erbium doped glasses have received a great deal of attention as fiber amplifiers for the 1.55 μm telecommunications window¹. Fiber gains in excess of 5 dB/mW of absorbed power with total gains greater than 35dB have been achieved in silicate glasses. However, it is always interesting to study the behavior of rare earths in glass hosts other than silicates and hopefully new features can be developed. Tellurite glasses have been chosen because they have very high indices of refraction (1.65-2.32), large nonlinear refractive indices (25 times higher than silica), and a relatively low phonon energy spectrum (peak values ~800 cm⁻¹). The absorption cross section for the hypersensitive transition ⁴I_{15/2}-²H_{11/2} does clearly indicate a difference for various Er concentrations.

This indicates a difference in site symmetry of Er ion in low and high concentrations. In this work we report local structure of the high concentration (2 wt%) glasses. The figure below shows the filtered first peak of radial distribution function of Er in glass. Er-O distance for this sample was 2.23 Å which is slightly smaller than the average Er-O distance of Er₂O₃. Number of oxygen atoms is hard to determine because of correlation between N and disorder term. But if we assumed same disorder as Er₂O₃ best fit gives 8 oxygen atoms. In the next step of the experiment we hope to do EXAFS of low (0.55 wt%) concentration Er glass.

++ Back transform data
-- One oxygen shell fit

References:

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Ga_{0.5}In_{0.5}P AND Ga_{0.5}In_{0.5}As THIN FILMS DEPOSITED ON GaAs STUDIED USING EXAFS

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Epitaxial MOCVD thin-film alloys of Ga_{0.5}In_{0.5}P and Ga_{0.5}In_{0.5}As grown on GaAs substrates have shown spontaneous long-range ordering and band gap reduction under particular growth conditions. A liquid nitrogen cooled total-electron-yield detector is used to investigate the EXAFS contribution of first, second and third nearest neighboring atoms in these single-crystal samples to determine the details of their short-range ordering.

Results from the gallium second nearest neighbor contribution in numerous Ga_{0.5}In_{0.5}P on GaAs samples have been scrutinized. One ordered sample, grown at 670 C, has revealed a sizable difference in the second nearest neighbor peak region at two perpendicular orientations of the sample crystal. These orientations highlight different atoms in the plane of growth indicating that different quantities of elements are present along different crystal axes. This result correlates to the (111) superlattice-type growth indicated by TEM measurements.

All other samples, grown at a variety of temperatures above and below the ideal growth temperature of 670 C, do not reveal significant differences in the second shell, although some samples emit TEM superlattice peaks, and all show some degree of band gap reduction. This may indicate that the percentage of domains of spontaneously-ordered material is small compared to other domains, but still significant to the band gap. Fitting has shown in some of these samples a predominance of disordering, and possibly a tendency for Ga to clump around Ga in the second shell. Samples with Zn added to cause deliberate disordering do not reveal a difference in the two orientations, as expected. More precise analysis is underway and results from recent EXAFS at Ga and As K-edge from Ga_{0.5}In_{0.5}As on GaAs will soon be presented also.

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SOLID PHASE REACTION BETWEEN COBALT AND SILICON-GERMANIUM ALLOY: AN EXAFS STUDY.

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The phase formation of Co reacting with Si_{1-x}Ge_x alloys has been studied by EXAFS. In this study, samples were prepared by depositing 200Å of Co on Si_{1-x}Ge_x (x = 0.20 and 0.30) alloy thin films in UHV and annealed in situ at different temperatures ranging from 400°C to 700°C for 20 minutes. The SiGe alloy thin films were epitaxially grown on Si(100) substrates by MBE.

Fourier transforms of Co K-edge EXAFS of annealed Co/Si_{0.8}Ge_{0.2} samples are shown in Figure 1. The shape of the EXAFS spectrum of samples annealed at 400°C, 500°C, and 600°C are similar to that of CoSi (FeSi structure) but with reduced amplitude. The increase of the amplitude with increasing annealing temperature indicates that the higher annealing temperature improves the crystalline quality of the reacted thin film, which has CoSi structure in this temperature range. For the sample annealed at 700°C, a new phase is formed (see Figure 1). Further analysis indicates that this phase has the some local atomic arrangement as CoSi₂ with slightly larger structural disorder. Our preliminary results suggest that Co mainly reacts with Si, and Ge is segregated from the original Si_{1-x}Ge_x alloys to form either Ge clusters or Ge enriched Si_{1-y}Ge_y (y>x) clusters. Further investigation is in progress.

Figure 1. Fourier Transform of Co K-edge EXAFS (k^2 weighted) of Co/Si_{0.8}Ge_{0.2} samples annealed at different temperatures. The transform range is from 3.0Å⁻¹ to 13Å⁻¹.

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MICROWAVE HEATING OF REACTION-BONDED SILICON NITRIDE

A. J. Allen & G. G. Long (NIST); and J. Thomas & D. L. Johnson (Northwestern U.)

A better microstructural understanding of sintering and processing in advanced ceramics would enable the achievement of better microstructural control and improved final product. Unfortunately, the pore sizes of interest are in the 0.1-2.0 μm size range, which is not tractable to small-angle scattering studies in the standard SAXS regime. For relatively dense material, the X23A3 USAXS facility combines short wavelengths with ultrahigh-resolution, and this permits the single-scattering curve to be determined with a minimum of multiple scattering.

The technique has been applied in studies of microstructure development in microwave-heated reaction-bonded silicon nitride (M-RBSN). Microwave heating to assist in the fabrication of RBSN offers a promising alternative processing route to conventional sintering of this technologically important refractory ceramic. In the formation of M-RBSN, porous silicon is progressively converted into silicon nitride by a microwave-assisted reaction with gas within the pores. Fig. 1. shows desmeared USAXS data as a function of h , while fig. 2. shows a preliminary scattering-feature volume size distribution, derived using maximum entropy analysis, from USAXS data in the h range: 0.005 to 0.2 nm^{-1} , for near 95% reacted material at approaching 80%TD. A bimodal distribution is revealed. The larger features are associated with the mean pore diameter obtained from multiple small-angle neutron scattering measurements (650nm diameter), and the size distribution derived from USAXS reveals this to be a broad gaussian population in size. The finer features dominate Porod scattering measurements of the surface area, and are probably associated with silicon nitride structures within the larger pores. Note the range of sizes probed by the USAXS facility which uniquely provides statistically representative and comprehensive information on the generic microstructures present in this material.

Fig. 1.

Fig. 2.

ULTRA-LOW Q AND PINHOLE SAXS OF CHLORINATED POLYETHYLENE.

G. Beaucage (Sandia Nat. Labs.), D. W. Schaefer (SNL), G. Long (Nat. Inst. Stds. and Tech.), D. A. Fischer (NIST), L. Effler (Dow Chemical), M. T. Berard (Dow Chemical).

We have recently measured ultra-low- q x-ray scattering data on polymers in which distorted crystalline structures occur. Chlorinated polyethylenes of high degrees of chlorination display very weak crystallinity. Ultra-low- q data are combined with the ORNL SAXS data in the figure below. The ultra-low- q data indicates the presence of structures in this low crystallinity material on the size scale of one micron. These structures have a fractally rough surface as is indicated by the power-law scaling of -3.4. A spherulitic structure is expected to display sharp interfaces which yields Porod type scattering with a power-law of -4. The absence of a correlation peak in any of the highly chlorinated PE's indicates very loosely packed lamellar structures. The buried R_g at high q may correspond with a lamellar dimension. Power laws close to -2 always follow this week R_g indicating distorted, randomly oriented lamellar scattering.

Fig. 1 Small-angle and ultra-small-angle x-ray data for chlorinated polyethylene.

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ULTRA-LOW Q SAXS AND CONVENTIONAL SAXS OF CARBON FILLED POLYETHYLENE COMPOSITES*

G. Beaucage (Sandia Nat. Labs.), D. W. Schaefer (SNL), G. Long (Nat. Inst. Stds. and Tech.), D. A. Fischer (NIST), K. Schwartz (Raychem Corp.).

A double crystal camera has been used to obtain ultra-low q SAXS data on a number of materials which display interesting structural scaling behavior. These data bridge the gap between static light scattering (SNL) and conventional pin-hole x-ray scattering (ORNL, SNL). We have recently investigated the structure of carbon filled composite materials in which polyethylene is the matrix material. The fit in figure 1 uses a unified Guinier/Power Law equation recently developed at Sandia. The scattering is described to a high degree of accuracy by a fractally rough particulate model which might be expected from carbon black aggregates. The rise in intensity at extremely low q may relate to structural features accessible in the light scattering regime. If one considers the scattering from PE crystallites to be completely independent from the scattering of the carbon black aggregates then a subtraction of the fit from the data is expected to yield a pattern which can be independently described by conventional lamellar models for PE. For the samples investigated to date this seems to be the case. The empty circles in figure 1 correspond very well with lamellar scattering from PE as can be seen in figure 2 where the subtracted data is compared to a PE standard. Neither of these data sets have been scaled. The crystallinity in sample 29-8 appears to be close to that of neat uncross-linked PE.

Fig. 1 Log-log plot of small angle x-ray data from Bonse-Hart and pinhole cameras. Fit is to a unified Guinier/Power Law equation.

Figure 2. Comparison of PE scattering pattern to that of the difference between sample 29-8 of 5% Raven 430 sieved powder and a fit to the carbon aggregate structure.

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CHARACTERIZATION OF A CVD-GROWN HOMOEPITAXIAL DIAMOND FILM

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A 95 μm thick diamond film was grown by microwave assisted CVD on a natural type IIa diamond substrate. The 5x5x0.1 mm³ substrate was characterized by x-ray diffraction imaging prior to growth of the film and a representative image is shown in figure 1. The majority of natural type IIa diamonds have undergone plastic deformation under geological conditions. This produces a high defect density, bending of the crystal lattice and a distinctive microstructure, called the "tatami" structure as seen in figure 1. The quality of this substrate was good for a sample selected essentially at random. The diffraction width, the range of Bragg angle required to have some part of the sample diffracting, was about 250 arcseconds prior to deposition. For comparison, diffraction widths as large as 2.8 degrees have been measured for other type IIa crystals. After deposition of the film, the diffraction image changed dramatically to that shown in figure 2. The diffraction width of the combination sample became ~1.1 degrees, which indicates the sample is bent to a radius of about 1.3 m. Bending after deposition is usually attributed to lattice parameter mismatch and/or a difference in coefficient of thermal expansion. The bending of this sample is surprising since for true homoepitaxy neither mechanism is possible. The cause of this deformation is currently under investigation.

Figure 1. 8 keV (220) symmetric transmission diffraction image.

Figure 2. Same as figure 1 after deposition.

X23A3

DIFFRACTION IMAGING OF AN ICOSAHEDRAL QUASICRYSTAL

David Black, NIST

Stefan Kycia and Alan Goldman, Ames Lab and Iowa State Univ.

Single crystals of face centered icosahedral $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ have been grown by the Bridgman technique. These crystal are sufficiently large, $2 \times 1 \times 1 \text{ cm}^3$, and sufficiently perfect so that the Borrmann or anomalous transmission effect can be observed¹ and therefore make ideal samples for diffraction imaging. A sample was prepared with a 2-fold surface by cutting and polishing with standard metallographic techniques. The 2-fold surface is particularly useful since symmetric transmission images can be obtained for all major symmetry directions, i.e. there are two orthogonal 2-folds, a 3-fold and a 5-fold on the circumference of the stereographic projection in the 2-fold direction. The diffraction image below is an enlarged area of a 5-fold symmetric transmission image obtained with 20 keV x-rays (the projection of the diffraction vector is vertical). Individual dislocations are clearly visible in the dark region (darker corresponds to higher diffracted intensity). The light region on the left has considerably higher defect density and is separated by a low angle grain boundary. A sharp grain boundary is seen at the top of the image. Dislocations are also seen to emerge from the grain boundary at the lower left corner.

0.5 mm

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X23A3

HIGH RESOLUTION DIFFRACTION IMAGING OF BGO THIN FILMS AND PHOTOREFRACTIVE FANNING IN BARIUM TITANATE

Gerard Fogarty and Mark Cronin-Golomb (Tufts U), Bruce Steiner (NIST), Uri Laor (NIST and NRC-Negev), and Arun Inam (Bellcore)

Figure 1 shows a (444) Bragg geometry image of a 0.5 micrometer BGO layer grown on a sapphire substrate. The rocking curve for this diffraction was extraordinarily wide (0.15° , FWHM), indicating a high degree of disorder. Despite this local disorder, the longer range order is sufficient for the layer to diffract simultaneously over a large portion of its surface. Cellular structure is clearly seen, along with irregular non-diffracting areas close to the centers of nearly all the cells. The cell walls appear to be approximately piecewise linear, and the cell size varies across the surface of the film. It is not yet known if cellular structure is typical of such films.

Figure 2 is a (002) Laue geometry image of a barium titanate sample exhibiting the photorefractive fanning effect. A 50 mW beam from a 532 nm

wavelength, frequency doubled YAG laser enters the 0.5 mm thick plate sample from the bottom of the image. Light scattered from imperfections within the crystal is amplified through the photorefractive effect, and "fans" out to one side of the main beam (the upper right in Figure 2). The photorefractive charge redistribution also causes lattice strain through the piezoelectric effect, which is visible as contrast changes in the upper right-hand portion of Figure 2.

Information from these images will be useful for refining models of the fanning effect, and in improving models of devices that rely upon fanning for their operation, such as self-pumped phase conjugate mirrors.

Figure 1: A (444) diffraction image at 10 keV in Bragg geometry of 0.5 micron BGO film on sapphire substrate, showing cellular structure.

Figure 2: A (002) diffraction image at 12 keV in Laue geometry of barium titanate sample exhibiting photorefractive fanning of laser beam entering from the [001] edge of the crystal.

This work was supported by the ARPA Optics Program through the Army Research Office.

HIGH RESOLUTION X-RAY DIFFRACTION IMAGING OF PHOTOREFRACTIVE SBN:60

Gerard Fogarty and Mark Cronin-Golomb (Tufts U.), Bruce Steiner (NIST), Uri Laor (NIST and NRC-Negev), and John Martin (Deltronic Crystal Industries)

High resolution diffraction imaging in Bragg geometry has been used to examine a small ($3 \times 3 \times 3.5$ mm³) sample of SBN:60 grown by Deltronic Crystal Industries. The sample showed remarkable long range lattice regularity for a solid solution system: it was possible to achieve diffraction over the entire crystal surface at certain points in the rocking curve for the diffractions observed (Figure 1).

Figure 1 also shows numerous quasi-regular striations running perpendicular to the [001] growth direction, the precise nature of which is presently unconfirmed, although certainly growth related. Close examination of this image reveals a sudden tilt of the striations suggestive of a low angle grain

boundary, and also reveals that the striations are slightly curved.

Figure 2, in which the diffraction vector is aligned with the growth direction, shows particularly interesting striations, indicative of an interface that was linear for some portions of the boule, and curved for others.

These preliminary images demonstrate both the achievement of lattice regularity at a level of arc seconds and the promise of diffraction imaging in tracing the origin of optically significant lattice features, such as striations, in SBN.

Figure 1: A (12 4 0) diffraction image at 8 keV in Bragg geometry of SBN:60 sample, showing growth striations. Growth direction is [001].

Figure 2: A (004) diffraction image at 8 keV in Bragg geometry of SBN:60 sample, showing curved and linear interface shapes.

This work was supported by the ARPA Optics Program through the Army Research Office.

SAXS OF ACTIVATED CARBON

Jeffrey FORTNER (Materials Science Division, Argonne Natl. Lab), Shiyu PEI (Amoco Research Center), and Pete R. JEMIAN (Dept. of Physics, Ill. Inst. of Tech.)

Small-angle X-ray scattering from a sample of activated carbon was measured to ascertain the nature of the extremely large surface area (per unit volume). Measurements of N₂ absorption indicate a surface area of 3000 m²·g⁻¹, larger even than the value expected if the material contained exclusively single graphite layers.

Attached is a figure showing data from the same sample measured on two different beam lines at the NSLS: X23A3 and X12B. On beam line X23A3, the collimation is by Bragg reflection approximating a long slit. The X12B instrument uses a series of apertures to collimate the beam resulting in a geometry approximating "pinhole collimation." Because the sample-to-detector distance was made small in the X12B experiment, to map the scattering at high Q , the Q -range overlap between the two instruments is small. The Q -range overlap is, however, sufficient to verify that the scattering recorded by the two instruments is reproducible.

It is observed that there are two very different length scales present in the activated carbon sample. This data is similar in appearance to that presented by Bale and Schmidt [1] from a sample of Beulah lignite. The data in the range of the X23A3 instrument is dominated by scattering from very large-scale features. This scattering has an observed dependence of Q^{-4} , signifying that the interfaces of the electron density inhomogeneities are "smooth" and not of a fractal nature, in contrast to the conclusions about the lignite [1]. At the largest Q -values measured in the X23A3 instrument, the scattering changes character due to the presence of very short length scales in the sample. This scattering is also observed by the X12B instrument. Preliminary analyses using the ITP program [2] indicate that the underlying scatterers from this sample have a distance distribution function, $p(r)$, which peaks at $r \approx 0.5$ nm.

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X23A3

CHARACTERIZATION OF THE BINDING OF GALLIUM, PLATINUM AND URANIUM TO *PSEUDOMONAS FLUORESCENS* USING SAXS AND TEM

S. Krueger and D. Johnsonbaugh (NIST), G.J. Olson (Little Bear Labs) and T.J. Beveridge (U. of Guelph)

Small angle x-ray scattering (SAXS) was used to determine the binding of Ga, U, and Pt to *Pseudomonas fluorescens* in aqueous buffer and TEM was used to determine the location of the cell-bound, metal precipitates as well as their size and physical structure. Energy dispersive x-ray spectroscopy confirmed the composition and identity of the precipitates and helped show them to be mostly associated with the envelope layers of the bacteria. Unlike Ga and Pt, which were exclusively located at the cell surface, U was also found intracellularly in ~10% of the cells. SAXS confirmed these results, discerning the bacteria as metal enshrouded particles 1.0-1.5 μm in diameter. SAXS also provided a statistically significant representation of the bound metal precipitates which ranged in size from 10 nm to 1 μm . The SAXS data suggested that Ga and U were spread over the entire cell envelope, whereas Pt was only associated with the external face of the outer membrane, as confirmed by the TEM images. In addition, the data showed that the distribution of U was ordered on at least two length scales corresponding to cellular (~0.5 μm) and intra-cellular (~50 nm) distances. This result was also confirmed by TEM, which showed that U formed needle-shaped particles which were aligned lengthwise within the cell envelope.

Overall, the correlation between the imaging and the scattering data was extremely good. Since SAXS is performed in an aqueous milieu, it yields a more representative picture of the physical state of the metal bound to cell surfaces.

Fig. 1. Log-log plot of the scattered SAXS intensity from Ga, U and Pt bound to *P. fluorescens* versus scattering vector Q . Data from NIST's high resolution SAXS beamline at the NSLS and NIST's 10 m SAXS instrument were combined to form one data set covering the range $0.004 \leq Q \leq 1.2 \text{ nm}^{-1}$. Measurable scattering was only observed for Pt over the range $0.003 \leq Q \leq 0.01 \text{ nm}^{-1}$.

X23A3

CAVITY EVOLUTION DURING TENSILE CREEP OF Si_3N_4
G. G. Long, W. Luecke, S.M. Wiederhorn and B. J. Hockey (NIST)

We have characterized the evolution of cavities during tensile creep of a Y_2O_3 -hot isostatically pressed Si_3N_4 , using precision density measurements, small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM). Our earlier SAXS measurements [NSLS Annual Report (1992) p. 363] indicated¹, rather unexpectedly, that the creep cavities are bimodally distributed in size. The larger population of cavities, which has long been recognized to exist, consists of lenticular 200 nm-size cavities which lie primarily on two-grain boundaries. Irregularly-shaped 500 to 1000 nm-size cavities, which are much more rare, were uncovered by means of the SAXS measurements. These were then found by TEM to lie at multigrain junctions. Although these larger cavities are much fewer in number, they account for approximately half of the total volume of cavities.

The present study was undertaken to follow the evolution of the cavities during creep in an effort to learn how they nucleate and grow. In an ideal experiment, it would be possible to determine the cavity volume fraction at various stages during the creep process on an individual specimen. In the technique we used, density, SAXS and TEM measurements were made on multiple specimens crept to various strains. All were tested at 1400°C and 125 MPa. The unfailed samples were crept for 3, 5, 15, and 90 hours, and the failed sample went for 364 hours. The SAXS results for the volume distribution of cavities in three of these samples are shown in Figure 1. We omit the data from two of the samples for clarity. It can clearly be seen that at first the .2 μm cavities increase in number, and then the larger cavities appear and grow as the strain increases to failure.

Figure 1. Volume fraction of creep cavities in Si_3N_4 .

1. W. Luecke, S.M. Wiederhorn, B.J. Hockey and G.G. Long, *Silicon Nitride Ceramics—Scientific and Technological Advances*, MRS Proc. 287 (1993) 487.

X-ray Diffraction Microscopy Images Associated with the Detailed Diffraction Pattern of a Y Ba₂ Cu₃ O_{7-x} Single Crystal

H.H. Schloessin, UWO, London, Canada, and R.D. Spal, NIST.

The lattice constants, a and b , in the orthorhombic phase of Y Ba₂ Cu₃ O_{7-x} differ by only 0.06 Å. Thus, on cooling from the high temperature tetragonal phase, the formations of twinned lattices with either {110} or {1 $\bar{1}$ 0} symmetry planes involving a nearly 90° lattice rotation about the c -axis and very low misfit strains, are energetically very favourable. Although thick twins with boundaries subtending small angles with the incident flux lines may increase the superconductor transition temperature, twinned lattices in the form of thin quasi-regularly spaced lamellae impede flux line penetration, reduce the limit of the critical current density and are thus undesirable. The {100} twins, at least at elevated temperatures, are piezocrescent and can be removed by cycling the temperature through the tetragonal/orthorhombic phase transition, at 600-650°C, under load. In the case of the crystal under study, this had been done with a uniaxial force applied to the b - c plane. Mechanical twinning and piezocrescence of twinned lattices play significant roles in the deformation of crystals in the brittle phase. Therefore, an untwinned 290 x 340 x 88 μm Y Ba₂ Cu₃ O_{7-x} crystal presented a most interesting and challenging case in ongoing diffraction microscopy studies of pressure figures in single crystals of different structures and compositions. Complete sets of O- and H-beam images, at 21x magnification and corresponding reflection curves recorded with varying θ or varying crystal azimuth at constant θ , were obtained for a large number of Laue-Bragg reflections. The images from all the different reflecting planes with the crystal in various azimuthal positions indicated that the untwining treatment was by and large successful in that it removed high concentrations of sizeable twin lamellae. However, the curves of both the 200 and 020 reflections exhibit component peaks with 87.42° azimuthal separation giving evidence of some residual and complementary twinned parts of the lattice with {110} and {1 $\bar{1}$ 0} symmetry planes. The lattice imperfections in the thermomechanically untwinned crystal are dominated by large-scale strain lobes and broad strain contours. The hourglass patterns of contrast seen in many of the images, may be due to the combined effects of residual microstresses caused by the uniaxial compression, the shape factor influence on the intensity scattered by the bounded prismatic volume, features inherited from possible hopper growth and stresses imparted by forces acting on the flux line lattice during high magnetic field exposure at low temperatures. Individually resolved defects include a few thin and straight deformation bands, curved segments of dislocation lines and loops and several rather large vacancy clusters forming tetrahedra. The latter most probably formed in the course of diffusion and gradual loss, of oxygen, which must attend the crucial order/disorder transformation in the occupancy of the lattice rows on the oxygen lattice. The present study also provides a complete pattern of the coherent scattering wave fields generated by Laue-Bragg reflections from the entire volume of a small bounded single crystalline particle. The Borrmann fan (energy triangle), generated by the interfering incident and scattered wave fields, with dimensions <500 μm at the crystal exit surface, exhibits an intensity distribution resulting from contributions of 2 largely wedge-shaped volumes overlapping with the contribution from a central prismatic volume. Owing to the deformations caused by the uniaxial contact forces, only very few pendellosung fringe patterns can be seen in the wedge-shaped regions. Many of the rocking curves exhibit multiple simultaneous reflections with very small angular separation. Images corresponding to both the separate and the merged diffraction peak positions were collected. The multiple reflections are also seen in photographs of the corresponding Laue spots. These and a very bright central anomalous transmission through the crystal, apparently associated with the twin reflection peaks, are still being investigated.

Fig. 1. 020 H-beam reflection micrographs at 21x magnification

X-RAY TRANSMISSION TOPOGRAPHY OF A THERMOMECHANICALLY DETWINNED, SUBMILLIMETER YBa₂ Cu₃ O_{7-x} CRYSTAL

R.D. Spal, D.L. Kaiser, F.W. Gayle (NIST) & H.H. Schloessin (UWO)

The microstructure of high- T_c materials is of special interest since it affects important superconducting properties such as critical current. X-ray topography is an ideal method for revealing this microstructure, if the material has sufficient perfection to permit anomalous transmission. In this study, transmission topographs were obtained of two submillimeter YBaCuO crystals grown from the melt. Their habit is a nearly perfect parallelepiped, aligned with the orthorhombic crystallographic axes. As grown, they were heavily twinned about {110} planes. One crystal was detwinned by uniaxial compression along an a/b axis at a temperature slightly below that of the orthorhombic to tetragonal phase transformation. The topographs were taken using an asymmetric Bragg diffraction microscope.

Figure 1 shows (200) and (020) 0-beam positive image topographs of the detwinned crystal, with the beam incident on the ab face, and with the plane of diffraction vertical. The crystal dimensions are 290 X 340 X 88 μm^3 along a , b , and c respectively. The optical thickness (μt) along c is 6.7 at the incident beam energy of 11.4 keV. Two-fold symmetric contrasting regions, bounded by the diagonals of the ab face, with strong transmission in the horizontally opposed quadrants and weak transmission in the vertical ones, suggest residual strain in the ab plane from the thermomechanical treatment. A search for the corresponding twin reflections found one tiny twin, about 30 X 30 μm^2 , near the center of the ab face. Finally, (200) 0-beam topographs of the twinned crystal, taken at several points through the rocking curve, reveal spatially uniform transmission at an untwinned corner composing about 10% of the crystal. The absence of contrast across the ab face diagonal at this corner shows that the strain in the detwinned crystal is not intrinsic to the melt growth.

Fig. 1. (200) and (020) 0-beam topographs of detwinned crystal

X23A3

INTERMEDIATE RANGE LATTICE UNIFORMITY IN SPACE-GROWN MERCURIC IODIDE

B. Steiner (NIST), U. Laor (NIST & NRC-Negev), and L. van den Berg (EG&G Energy Measurements)

The mercuric iodide crystal vapor-grown on space shuttle IML-1 displays uniformity in intermediate range lattice orientation, *i.e.* on a scale comparable to the 1 mm thickness of the crystal slice, a factor 10 - 20 higher than a comparable crystal grown on the ground. Figure 1 contains a high resolution monochromatic diffraction image of a slice of the IML-1 crystal, while Figure 2 contains a similar image of a comparable terrestrial crystal. The regions in diffraction in the IML-1 crystal shown in Figure 1 are clearly a factor of 10 - 20 wider than those in the terrestrial crystal shown in Figure 2, reflecting a comparable increase in uniformity in lattice orientation on a scale comparable to the distance to be travelled by charge carriers in detectors made from such crystals. The terrestrial crystal was grown in a manner similar to that used on IML-1 from identical material.

Figure 1. Single (008) diffraction image of a slice of the mercuric iodide crystal grown on IML-1. The image was taken in Bragg geometry at 8 keV. The area in diffraction is a factor of 10 - 20 wider than that for the comparable terrestrial crystal, shown in Figure 2, indicating that the lattice is comparably more uniform in intermediate range orientation than that of the terrestrial crystal.

This work was sponsored by the NASA Microgravity Sciences and Applications Division.

This increased uniformity in the orientation of the lattice in the IML-1 crystal on a scale comparable to the charge carrier travel distance fulfills the principal expectations for this space crystal growth experiment. Mercuric iodide is extremely soft at crystal growth temperature and thus particularly susceptible to hydrostatic loading by gravity. Reduction of this loading by growth on IML-1 resulted as expected in more uniform lattice orientation than that achieved with comparable material on the ground. These observations parallel closely those of the overall lattice uniformity in the accompanying superimposed multiple diffraction images. More important, the expected improvement in the electrical parameters of radiation detectors made from other slices of these crystals, which are expected to be particularly sensitive to lattice regularity over the distance travelled by charge carriers, has been achieved. The superior electrical properties of these crystals result, in turn, in an increase in energy resolution for the detectors made from them.

Figure 2. Single (008) diffraction image of slice of comparable terrestrial crystal grown from IML-1 material, in Bragg geometry at 8 keV.

X23A3

OBSERVATION OF ANOMALOUS DIFFRACTION THROUGH MERCURIC IODIDE CRYSTAL IN LAUE GEOMETRY AT 11 KEV

B. Steiner (NIST), U. Laor (NIST & NRC-Negev), & L. van den Berg (EG&G Energy Measurements)

Anomalous diffraction through a mercuric iodide crystal in Laue geometry at 11 keV has been observed for the first time. Figure 1 contains a (020) high resolution diffraction image of a newly grown mercuric iodide crystal in Laue geometry at 11 keV, while Figure 2 contains a similar (200) image. Both figures show comparable O and H images, demonstrating that the radiographic transmission of higher energy radiation plays a negligible role in these images, which required careful rejection of 33 keV harmonics. The region in transmission is limited within the respective images by residual variation in the lattice and at the periphery by slits arranged to cut scattering close to the edges of the crystal.

The achievement of the crystal regularity necessary for the observation of anomalous transmission depended on the two factors: extraordinary purification of the starting material and the development of special crystal handling techniques for dealing with the resulting lower yield strength of the crystal. Identification of the features observed will depend on the achievement of asymmetric transmission, which has not yet proved possible, due to the additional path length required and the heavy atomic weights of the atoms.

Figure 1. High resolution images of (020) diffraction through high purity 0.5 mm thick mercuric iodide crystal in Laue geometry at 11 keV. The comparable irradiance of the lower O beam image and of the upper H beam image shows that radiographic transmission plays a negligible role in the lower image.

Figure 2. High resolution images of (200) diffraction through high purity 0.5 mm thick mercuric iodide crystal in Laue geometry at 11 keV. The comparable irradiance of the lower O beam image and of the upper H beam image shows that radiographic transmission plays a negligible role in the lower image.

This work was supported by the NASA Microgravity Sciences and Applications Division.

OVERALL LATTICE UNIFORMITY IN SPACE-GROWN MERCURIC IODIDE

B. Steiner (NIST), U. Laor (NIST & NRC-Negev), and L. van den Berg (EG&G Energy Measurements)

The mercuric iodide crystal vapor-grown on space shuttle IML-1 displays uniformity in overall lattice orientation a factor of fifteen higher than that of a comparable crystal grown on the ground. Figure 1 contains seven superimposed high resolution monochromatic diffraction images of a slice of the IML-1 crystal as it is rotated in Bragg angle in successive steps of 0.01° . By this means, nearly all of the crystal can be brought into diffraction over a range of 0.07° . In strong contrast to this uniformity of the lattice orientation in the IML-1 crystal, variation in the orientation of the lattice in a comparable terrestrial crystal requires that the crystal be rotated by 20 steps of 0.05° for it to be brought into a comparable degree of diffraction, shown in Figure 2. The terrestrial crystal, grown in a manner similar to that used on IML-1 from identical material, thus varies in lattice orientation by more than 1° .

Figure 1. Five superimposed (008) images of a slice of the mercuric iodide crystal grown on IML-1. The images were taken in Bragg geometry at 8 keV as the crystal is rotated in Bragg angle in steps of 0.01° . The overall crystal lattice is thus a factor of fifteen more uniform in orientation than that of the comparable terrestrial crystal, shown in Figure 2.

Figure 2. Twenty multiple (008) images of slice of comparable terrestrial crystal grown from IML-1 material, in Bragg geometry at 8 keV as the crystal is rotated in Bragg angle in steps of 0.05° .

This work was sponsored by the NASA Microgravity Sciences and Applications Division.

PRECIPITATION HARDENING IN NEWLY AVAILABLE HIGHLY PURIFIED SINGLE CRYSTALS OF MERCURIC IODIDE

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Single crystals of mercuric iodide recently grown from newly available highly purified source material demonstrate precipitation hardening in those regions that grew in the $[110]$ direction, and its absence in those that grew in the $[001]$ direction.

Figure 1 is a high resolution diffraction image of a 1 mm thick slice of such a mercuric iodide crystal carefully cut and incompletely polished in order to minimize rearrangement of the lattice through this treatment. Before cutting, the growth of this region of the crystal had been observed to be in the $[001]$ direction. Figure 2 is a similar image of a 0.5 mm slice of another region of the same crystal, similarly cut and incompletely polished in order to minimize rearrangement of its lattice. This slice was cut to include part of the crystal that had grown in the $[001]$ direction (the upper part of Figure 2) and another that had grown in the $[110]$ direction (the lower part of Figure 2).

Figure 1. High resolution (008) diffraction image of 1 mm thick slice of a portion of mercuric iodide crystal that grew in the $[001]$ direction.

The lower part of Figure 2 is observed to differ from that of the upper part in two important ways. First, the lower part has small linear arrays of inclusions, which are out of diffraction, while the upper part is relatively free of them. Second, the orientation of the lattice of the matrix in the lower part is sufficiently uniform that all regions are simultaneously in diffraction, while the orientation of the lattice of the upper part varies enough to prevent diffraction simultaneously in all regions.

The upper part of the 0.5 mm thick crystal imaged in Figure 2 is generally comparable to the 1 mm thick crystal imaged in Figure 1. Thus, the inclusions observed harden the lattice of the thinner crystal sufficiently to prevent its deformation under conditions that clearly do deform the region that is not precipitation hardened. The nature of these inclusions remains to be determined.

Figure 2. Comparable (008) diffraction image of a 0.5 mm thick slice of another portion of the same crystal, the upper part of which grew in the $[001]$ direction, while the lower part grew in the $[110]$ direction. Precipitation hardening is evident in the lower portion, in which arrays of inclusions are visible.

This work was supported by the NASA Microgravity Sciences and Applications Division.

SENSITIVITY OF LATTICE REGULARITY IN MERCURIC IODIDE SINGLE CRYSTALS TO RECENT INCREASES IN PURIFICATION

B. Steiner (NIST), U. Laor (NIST & NRC-Negev), and L. van den Berg (EG&G Energy Measurements)

The uniformity of lattice orientation in recently available, highly purified mercuric iodide single crystals has been shown to be sensitive to crystal handling techniques that did not affect the regularity of previously available high purity single crystals. This regularity, in turn, can have profound effects on the electrical properties of these crystals.

Mercuric iodide single crystals are of particular interest as energy sensitive radiation detectors because they operate with high sensitivity at room temperature. Special cutting and polishing techniques were developed several years ago to ensure that this sensitivity was not compromised by the extraordinarily low yield strength of this material. However, recent success with increased purification procedures has led to unanticipated increases in sensitivity to cutting and polishing.

Figure 1. Multiple (008) diffraction images of highly purified mercuric iodide crystal in Bragg geometry at 8 keV. The crystal had been cut and polished by techniques shown to be suitable for previously available material. Here the crystal was rocked 0.05° in Bragg angle between successive images.

Figure 1 shows superimposed multiple high resolution diffraction images of a crystal grown within the last year from newly available source material and then cut and polished with techniques that had previously been demonstrated through high resolution diffraction imaging not to affect the lattice regularity of earlier crystals. Most of the area of these earlier crystals could be brought into diffraction at a single (Bragg) angle with respect to the incoming beam. In the present instance, however, the crystal had to be rotated 0.05° in the Bragg direction between successive images, leading to six distinct images.

Figure 2 shows a similar diffraction image of a crystal cut and polished by generally similar techniques, but modified by taking into account the possibility of substantial reduction in yield strength. In this case, a single orientation of the crystal enables most of it to diffract under conditions comparable to those of Figure 1. Planar arrays of inclusions, viewed edge-on, delineate the faceted growth mode of this material. The inclusions have resisted chemical analysis to date.

Figure 2. Single (008) diffraction image of similar crystal cut and polished taking into account the possibility of yield strength lowering with increased purification.

DIFFRACTION IMAGING OF QUARTZ RESONATOR STRUCTURES

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Quartz crystal piezoelectric devices have benefitted from the development of synthetic growth processes which reproducibly yield crystals of controllable purity and with lower dislocation densities than naturally occurring samples. Despite the advances already made, further improvements are thought to be possible for certain types of devices. In particular, we are seeking a correlation between operational characteristics and observable strains, such as surround extended defects, in test structures fabricated from high quality synthetic α -quartz material. A correlation, once established, can be a guide to further scientific and engineering progress.

In preparation for experiments with operable devices, we have imaged the strains in selected devices by monochromatic x-ray diffraction imaging on NSLS Beam Line X23-A3. The high resolution of this beam line fully engages the resolving power of the best optics used in microscopes and photographic equipment by which the images are viewed or printed for analysis. The suite of diffractions includes symmetric and asymmetric planes, in surface and in transmission diffractions, in as many of the three orthogonal zones as are accessible.

We have examined the resulting images for lattice imperfections in the devices. Dislocation line densities in the devices are in the range of about a hundred per square centimeter and below. Individual threading dislocations can be viewed by diffracting the x-ray beam in transmission through the quartz structure. The test structures are sufficiently small in cross section that two orthogonal transmission views may be taken of the same region. The images demonstrate that not all lattice imperfections extend completely through the structures. Occasionally, groups of extended defects are found, presumably introduced during the lapping, polishing, and etching process by which the crystals are reduced in thickness.

The overall shape of the test structures is sometimes found to be modified by etch channels, such as can occur when a threading dislocation at an edge of the structure is contacted by the etching solution. These show clearly in surface diffractions, which also register surface texturing remaining from the sample preparation procedures.

In addition to dislocations, we also see macroscopic strains, some of which are warpage from process-induced surface damage. Warpings of over 30 times the diffraction peak width (≈ 10 arc sec) have been measured on the beam line. We have verified that the warpage is removed by etching the damaged surface layer away.

The analysis of the plates continues. Correlation between extended lattice defects and device operation will be explored. Measurements of the operational parameters by specialized instrumentation involving piezoelectric pickups on the crystal itself are planned. Device performance before, during, and after operation will be compared with x-ray diffraction images taken at the same time.

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SPECULAR REFLECTIVITY MEASUREMENTS FROM LANGMUIR-BLODGETT FILMS OF A SIDE-CHAIN POLYMER

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The specular reflectivity of synchrotron x-rays from Langmuir-Blodgett multilayer films of a side-chain polymer has been measured. The polymer (RP49) consists of a poly(methylmethacrylate) backbone with 4'-methoxybiphenyl pendant mesogenic groups and oligo(ethylene-oxide) flexible spacers ($M_w=183,000$). It has been shown that Langmuir-Blodgett multilayers of certain polysiloxane side-chain polymers can be transferred to solid substrates wherein the polymer side chains reorient upon transfer to form a one-dimensional unit cell very close to that of the bulk liquid-crystal phase. This results from the inherent flexibility of the polysiloxane backbone, and the liquid-crystallinity of the side chains at room temperature. Stable monolayers of RP49 prepared at the air-water interface of a Langmuir trough were transferred to an OTS hydrophobized silicon substrate to study the effects of the methacrylate backbone stiffness on side-chain reorientation.

The specularly reflected x-ray intensity from a 50-layer Langmuir-Blodgett film of RP49 is shown in Fig. 1. A single Bragg feature is evident near $0.45 \text{ \AA}^{-1}$ along with Kiessig fringes due to interference from x-rays reflected from the film and silicon surfaces, respectively. Detailed analysis yields a film with thickness $D=678.2 \text{ \AA}$ possessing a sinusoidal density wave which decays exponentially from the substrate with a decay length L of $451 \text{ \AA}$. The periodicity of this density wave is $14.4 \text{ \AA}$ which does not correspond to the bulk layer spacing ($29.8 \text{ \AA}$). The density wave has a 0° phase with respect to the surface of the OTS. We conclude that the side chains do not appreciably reorient to assume a bulk-like orientation, but rather maintain glassy conformations more closely related to the monolayer structure. It is likely that the side chains are oriented at an oblique angle with respect to the normal of the water surface resulting, after transfer, in a layer spacing much less than the molecular length.

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SUBSTRATE TEMPERATURE DEPENDENCE OF STRUCTURAL ANISOTROPY IN AMORPHOUS TB-FE

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We have performed polarization-dependent extended X-ray absorption fine structure measurements on a series of amorphous Tb-Fe films grown at different substrate temperatures. These TbFe films have a strong perpendicular magnetic anisotropy which increases with the temperature of the substrate during growth [1]. The atomic environment of the Fe atoms were probed along both the in-plane and out-of-plane directions by utilizing the polarization properties of synchrotron radiation and the sensitivity of EXAFS to polarized radiation. EXAFS modeling analysis was performed using the FEFF v.3.11 EXAFS codes [2] together with empirical standards.

A local structural anisotropy was detected between the in-plane and out-of-plane structure around the Fe atoms. This anisotropy is identical to the anisotropy described earlier by Harris et al. [3]. Figures 1 (a), (b), and (c) are Fourier transformed Fe EXAFS data collected from $Tb_{26}Fe_{74}$ films deposited at substrate temperatures of 77K, 300K, and 525K, respectively. These data show the anisotropy as differences in the amplitude and shape of the near neighbor Fourier peak. Modeling analyses of the near neighbor Fourier peak region indicate the existence of anisotropic pair correlations where Fe-Fe pairs are statistically preferred parallel to the film plane and Fe-Tb pairs are preferred along a direction perpendicular to the film plane. The measured pair correlations are found to increase in proportion to the magnetic anisotropy energy as a function of the substrate temperature. We believe these preferred atomic arrangements form during growth (similar to the mechanism described in ref. 1) and create an anisotropic electrostatic field distribution at the Tb sites. The aspherical charge cloud of Tb couples to the electrostatic field providing a strong local magnetic anisotropy which because of this structural anisotropy manifests as a large macroscopic effect.

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Figure 1. Fourier transformed Fe EXAFS data collected from amorphous $Tb_{26}Fe_{74}$ films deposited at (a) 77K, (b) 300K, and (c) 525K using normal and glancing angle radiation for samples.

POLARIZATION-DEPENDENT EXAFS MEASUREMENTS OF COCR FILMS

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Sputter-deposited Co-Cr films have proven useful materials for perpendicular magnetic recording applications. Although the literature is replete with studies of the properties of this material, aspects of its microstructure remain unclear. Two models have been proposed to account for the observed magnetic behavior: the Co-rich core model (Cr segregation at the column boundaries) and the CP model (compositional separation within the columns).¹ However, little experimental data exists which supports any one model. In order to address this issue we have applied polarization-dependent extended x-ray absorption fine structure (PD-EXAFS) to study well-characterized $\text{Co}_{0.78}\text{Cr}_{0.22}$ film samples.² When the polarization dependence of EXAFS is utilized, this technique serves as an element specific, local structural probe which allows for the independent measurement of in-plane and out-of-plane structure in film samples.

The extended fine structure appearing above the absorption edges was measured using normal and glancing incident radiation, allowing for the independent sampling of the in-plane and out-of-plane structure around both constituents. Standard EXAFS analysis procedures were followed leading to element-specific radial distribution functions.

The Fourier transformed Co and Cr EXAFS data are presented as Figure 1. These spectra illustrate an unambiguous structural anisotropy between the in-plane and out-of-plane structures. The in-plane structure around both constituents has characteristics of a close-packed atomic symmetry, consistent with x-ray diffraction studies which show the presence of a highly textured, hexagonal close-packed structure. In contrast, the out-of-plane structure illustrates a significant degree of disorder in the higher-order neighbors. Specifically, the Fourier peaks corresponding with the third and fourth neighbors of the close-packed unit cell are significantly reduced in amplitude, while the near neighbors and next near neighbors show little anisotropy in their radial distance or Fourier amplitude. The increased disorder of higher shells occurs in the out-of-plane structure relative both Co and Cr atoms and cannot result from the columnar growth morphology common to these films. EXAFS modeling procedures using multiple-scattering FEFF codes are in progress and should provide insight into the local chemistry and structure of the higher-order shells around Co and Cr atoms.

Figure 1. Fourier transformed Co (upper panel) and Cr (lower panel) EXAFS data collected from a $\text{Co}_{0.78}\text{Cr}_{0.22}$ sputtered film using normal and glancing incident radiation.

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STRUCTURAL EVOLUTION OF HEAT-TREATED CuCo POWDERS PROCESSED VIA CHEMICAL MEANS

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Powder samples consisting of Cu and Co metals were fabricated by a chemical co-precipitation technique. [The atom ratio of Cu to Co was 4:1.] Originally precipitated as Co- and Cu-hydroxides, samples were heat treated under flowing H_2 gas to obtain a metallic CuCo alloy. The structural evolution of the powders as a function of heat treatment was measured using extended X-ray absorption fine structure and X-ray diffraction.

X-ray absorption spectra encompassing the Co and Cu K absorption edges were collected using the NRL X23B materials analysis beamline in transmission mode. Standard EXAFS analysis procedures were applied leading to Fourier transformed data. Figures 1 (a) and (b) illustrate Fourier transformed Co EXAFS data for samples annealed at temperatures ranging from 200-500°C. The Fourier transforms were performed using k-ranges of $2.3\text{--}14\text{Å}^{-1}$ with a k^2 -weighting. The Fourier peaks are labeled as either neighbors in the fcc metallic phase, superscript 'm'; or neighbors in an oxide phase, superscript 'o'. The subscript indicates the order of the coordination shell. This information was deduced from comparison to Fourier transformed EXAFS data collected from empirical standards of Cu, $\text{Co}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$, and Cu_2O samples.

In Fig. 1 the Co environment is observed to change from an oxide state (200°C) to a mixture (250°C) of oxide and close-packed metal with the close-packed metal features dominating the spectrum. Because no fcc diffraction features are seen in XRD for a Co metal phase we believe that the Co exists within the Cu fcc phase. After an anneal at 300°C (panel (b)) the Co environment resembles that of the fcc Cu standard (not shown) with the first four neighbors of the fcc structure identified in the spectrum. X-ray diffraction measurements still only show a single set of fcc diffraction features corresponding to the Cu phase. A shoulder on the smaller d-spacing side of the Cu peaks suggests that Co within the Cu matrix is beginning to phase separate in this sample. An anneal at 500°C leads to an increased amplitude and resolution of the features in the Fourier transformed EXAFS data, consistent with the coarsening of fcc crystallites. The XRD pattern for this sample illustrates a second set of diffraction features at d-spacings consistent with a Co-rich fcc phase signaling the phase separation of Co from the Cu matrix.

These results illustrate how metastable alloys of immiscible elements can be formed via a chemical co-precipitation and reduction technique.

Figure 1. Fourier transformed Co EXAFS data for CuCo powder samples annealed at 200°C, 250°C, 300°C, and 500°C. The inset schematic to panel (b) correlates the Fourier peaks to the lattice positions in the fcc unit cell.

EFFECT OF ACRYLAMIDE AND DODECANE ON THE BICONTINUOUS CUBIC PHASE OF MONOOLEIN*

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Many lipid-water systems are known to display a rich variety of liquid crystalline phases that include lamellar, hexagonal and bicontinuous cubic phases. In the bicontinuous cubic phase, a convoluted lipid bilayer divides space into two disconnected but continuous regions. The phase which consists of multiconnected uniform nanopores and a large interfacial area, can be stabilized by polymerizing monomers in the aqueous regions. We have studied the phase behavior of monoolein as a function of acrylamide, a polar monomer which can be polymerized by free radical polymerization. We find that acrylamide binds strongly to the glycerol headgroup, increases head-head repulsion, and dramatically decreases the range of stability of the cubic phase. In addition, as shown in the figure with increasing acrylamide concentration, the unit cell increases and the sample exhibits a transition from a more curved double diamond phase with Pn3m symmetry to the gyroid phase with Ia3d symmetry. The ratio between the unit cell dimensions is 1.57 which is in good agreement with the theoretical ratio for this transition. This effect was counteracted and the cubic phase regained by the addition of dodecane. With the addition of dodecane, the behavior is exactly opposite to that observed with the addition of acrylamide. Dodecane being hydrophobic partitions between the tails, increases their disorder, and tail-tail repulsion. This counteracts the enhanced head-head repulsion due to the addition of acrylamide and stabilizes the cubic phase.

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Simultaneous Small-and-Wide-Angle X-ray Diffraction from Liquid Crystals as a function of variable temperature

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The phase transitions of liquid crystal require structural information both in terms of long range and short range orders and as a function of variable temperature. A system is developed which would allow us to obtain small angle and wide angle diffraction information on image plates with appropriate slit system as the temperature is varied. Both the image plates for the small angle and the wide angle are coupled together as they are translated behind the slit system while the temperature of the sample is changed at a known rate. By knowing the initial and final temperature for the translation of image plates from initial to final position and by knowing the rate of increasing the temperature and the translation of image plates, the phase diagram of liquid crystal phase transitions could be mapped in real time. The following figure shows the schematic configuration of the setup.

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Phase Transition Mechanisms in Mixed Phospholipid Dispersions

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Biological membranes consist of mixtures of a variety of lipid molecular species. It is therefore relevant to examine mixed lipid systems and dispersions of binary mixtures of dioleoylphosphatidylethanolamine and dioleoylphosphatidylcholine which have been studied in some detail because they reflect the existence of both bilayer-forming and non-bilayer forming lipids in biomembranes. Dispersions of these lipids in differing molar ratios, for example, are known to exhibit complex phase behavior including the tendency to form an intermediate cubic phase as judged by ³¹P-NMR and X-ray diffraction measurements. The present work extends these observations using dynamic X-ray diffraction measurements combined with differential scanning calorimetry and freeze-fracture electron microscopy to examine a mixed dispersion of dioleoylphosphatidylethanolamine/dioleoylphosphatidylcholine (3:1, wt/wt) dispersed in excess water. The particular feature that we wished to examine was the transition from lamellar to non-lamellar phase that takes place around 55°C as there had been an indication from the freeze-fracture and thermal studies that an intermediate cubic phase may be feature of the transition mechanism. Temperature scans were performed in heating mode between 25 °C and 65 °C and diffraction patterns recorded through the transition by translating an image plate behind a mask. A reasonable resolution of the structural change from lamellar to non-lamellar phase was observed and this appeared to be consistent with a transition from a liquid crystalline lamellar phase directly to hexagonal-II structure with no convincing evidence for an intermediate cubic phase. Further studies are in progress to improve the resolution even more by devising a thermal protocol that establishes the greatest possible order within the phases during the transition process.

X23B

Interdigitated Ripple Structures in Phosphatidylcholine-Cholesterol Multilamellar Systems

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The existence of an undulated or ripple phase in a variety of lipid and lipid/cholesterol systems has been well documented in recent years [see for example Ref. 1]. The present work extends these observations using dynamic X-ray diffraction measurements. The particular feature that we wished to examine was the temperature and hydration dependence of the ripple phase in phospholipid-cholesterol multilamellar systems with and without various salt solutions. Samples were subjected to heating scans and X-ray diffraction measurements were taken during the scan by using a movable mask in front of an image plate. Interdigitation of lamellar phases in pure lipid systems through the use of salt solutions, in particular KSCN and ethanol solutions, in the aqueous phase has been recognized as a unique packing of the lipid acyl chains. A dynamic thermally induced interdigitated ripple structure was observed for fully hydrated mixtures of dipalmitoylphosphatidylcholine plus 5 mole % cholesterol in the presence of KSCN or ethanol/water solutions. The coexistence of both ripple and interdigitation signatures represents a previously unknown geometric phase. The interdigitation tends to increase the ripple wavelength by approximately 10-30% over that found for the same systems without the addition of salts.

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X23B

Structural Examination of the High-Enthalpy Pretransition in Binary Mixtures of DMPC and DMPG

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We investigated the dynamic phase structures of binary mixtures of dimyristoylphosphatidylcholine (DMPC) and dimyristoylphosphatidylglycerol (DMPG) using real-time X-ray diffraction. A previous calorimetry study [1] reported a pretransition in binary mixtures of DMPC and DMPG which had an extraordinarily high transition enthalpy, nearly an order of magnitude higher than those values previously found for similar transitions. It was hypothesized that this transition was most likely due to the formation of a hydrogen bond between the head groups of the two phospholipid species in the gel (L_{β}') phase which is disrupted at the transition to the ripple (P_{β}') phase. We were interested in determining if any structural changes occurred in either the L_{β}' phase or the P_{β}' phase in these lipid systems that would explain the high enthalpy pretransition. Temperature scans were performed in a heating mode between 10° and 30°C and diffraction patterns were recorded through the transition on a translating image plate behind a mask. Phase transition temperatures were consistent with the previously reported values. The phase structures for equimolar mixtures of DMPC and DMPG were found to be different from pure DMPC suggesting that the high enthalpy pretransition may arise from these structural differences. Further studies to confirm these results are in progress.

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PERFORMANCE OF InSb/KDP MONOCHROMATOR CRYSTAL PAIR

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ABSTRACT

We report on the performance of an KDP/InSb monochromator mismatched crystal pair in use on beamline X24A. This crystal pair provides extremely high spectral resolving power and throughput in the photon energy range 1750 to 2100 eV, which is below the physical limit of Si(111). By measuring the back reflection from a Si(111) single crystal, we determine the resolution of the mismatched pair to be 0.40 ± 0.05 eV at 1977 eV.

The following figure shows the silicon 1s absorption spectra recorded with the KDP/InSb monochromator crystal pair compared to similar data recorded at SSRL using two InSb crystals. Note the enhanced resolution.

X24A

X-ray Standing-Wave Study of Surface Relaxation on the Ionic CdTe(110) Surface

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The x-ray standing-wave technique through the detection of surface-sensitive Auger electrons has determined the surface reconstruction of the strongly ionic CdTe(110) surface. Using the back-reflection diffraction geometry from (220) planes, our data indicate that, contrary to recent theoretical calculations, the relaxation is independent of the semiconductor ionicity. Rather, the strongly ionic CdTe crystal yields the same anion-cation bond angle rotation of 27 degrees as found previously by the same technique for the more covalent InP.

Satellite Structure in the Argon 1s Photoelectron Spectrum

X-24A

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Atomic inner-shell photoelectron spectra typically display several relatively weak "satellite peaks" at higher ionization energy than the primary peak. Satellite peaks are associated with final state configurations corresponding to ionization of an inner-shell electron and excitation or ionization of one or more valence electrons. The observation of satellite peaks demonstrates that the independent-electron picture is inadequate to describe atomic structure and the photoionization process [1]. The measured energies and intensities of photoelectron satellites provide sensitive tests for the development of many-electron theoretical models.

The figure shows the Ar 1s photoelectron spectrum recorded on beamline X-24A at an x-ray energy of 3628 eV. The primary peak at 3206 eV ionization energy was recorded at an observed resolution of 1.8 eV (FWHM). The satellite structure shows remarkable similarity to that recorded in the suprathreshold region of the Ar K photoabsorption cross section [2], which has been the subject of several theoretical studies [3].

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ADSORPTION SITE INVESTIGATION OF Rb/Cu(111) USING THE X-RAY STANDING WAVE METHOD

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We have carried out a Normal Incidence X-Ray Standing Wave investigation to study the adsorbate bonding sites for the system Rb/Cu(111). Our LEED study showed an ordered (2x2) phase for one monolayer of Rb on Cu(111). By measuring both the (111) and (11 $\bar{1}$) Bragg reflections at this coverage, we obtained Rb-Cu spacings of $3.08\text{\AA} \pm 0.01\text{\AA}$ relative to the (111) plane and $1.08\text{\AA} \pm 0.03\text{\AA}$ relative to the (11 $\bar{1}$) plane. Based on these triangulation measurements, we determine the Rb adsorption to be in the *top* site. The effective radius for the adsorbed Rb atoms is $1.80\text{\AA} \pm 0.01\text{\AA}$, closer to the ionic ($1.48\text{\AA}$) than the metallic ($2.43\text{\AA}$) value.

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SOFT X-RAY LUMINESCENCE OF POROUS SILICON

E. L. Benitez, D. E. Husk, and S. E. Schnatterly (University of Virginia)

Porous silicon has been a topic of great interest recently. We have measured the relative visible luminescence efficiency (visible photons out per soft x-ray photon in) as a function of soft x-ray excitation energy for a variety of porous silicon samples. The energy region containing the silicon $L_{2,3}$ edge is of particular interest. Using the absorption spectra of some possible constituent materials, we analyzed the energy dependence of the photoluminescent efficiency in terms of recombination of carriers at the surfaces and interfaces of the material, as we have done earlier with other materials.¹

The efficiency was modeled in terms of three elements: an SiO_2 overlayer, which absorbs photons and emits no light; a luminescent layer, which is assumed to be silicon based and converts soft x-rays into visible light; and a Si substrate, in which absorbed photons generate charge carriers which may diffuse into the luminescent region. This model is fairly successful, and indicates an SiO_2 overlayer microns thick on our samples. Most interesting is that we obtained our best fits for the luminescent layer by using a silicon absorption spectrum shifted 0.8 eV upward. This shift appears to be too small to be due to a silicon-oxide-based luminescent compound, but may be consistent with quantum confinement² or surface states³ models of porous silicon photoluminescence.

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X24C

CHARACTERIZATION OF SILICON BONDING ON RECONSTRUCTED SiC(100) SURFACES USING HIGH-RESOLUTION Si 2p SOFT-XRAY PHOTOEMISSION

V.M. Bermudez and J.P. Long (Naval Research Lab.)

Thin films of δ SiC for use in electronic devices are grown by CVD on Si(100) substrates. Microscopic surface chemical imperfections and local strain are important and are best addressed using core level SXPS. Samples, provided by L. Matus (NASA-Lewis), were cleaned by annealing in UHV in a Si flux, giving a (3x2) LEED pattern due to a partial monolayer of Si adsorbed on the terminating Si layer of the SiC lattice. Desorbing this "excess-Si" layer gives a (2x1) structure like that of Si(100). Exposing the (2x1) (but not the (3x2)!) to C_2H_4 at $\sim 1000^\circ C$ gives a c(2x2) structure terminated in a monolayer of carbidic C.

Fitting a gaseous Kr 3d spectrum gives an instrumental width of $\Gamma_c = 0.3$ eV. The main c(2x2) peak arises from underlayer Si and the satellite from unreacted Si on the initial (2x1) surface. Reaction with C_2H_4 titrates surface Si atoms in the (2x1) phase, revealing small excess-Si areas not detectable by LEED or Auger. For the (3x2), bulk ("B") and surface ("S") peaks are identified via the dependence of intensity on $h\nu$ and electron escape angle (ϕ_e). The "S"/"B" ratio indicates a 2/3-monolayer "excess-Si" coverage, consistent with a missing-row dimer model. The peak widths (~ 0.7 and 0.9 eV for "B" and "S") suggest substantial strain.

X24C

SOFT X-RAY RESPONSE OF POROUS SILICON PHOTODIODES

D. E. Husk, E. L. Benitez, and S. E. Schnatterly (University of Virginia)

The photoresponse of two aged porous silicon photodiodes (made by method in ref. 1) in the soft x-ray regime (160-550 eV) was measured (Fig. 1). The absolute quantum efficiency for the photodiodes was measured and the features observed in the efficiency spectrum were determined to be caused by the absorbed/reacted atmospheric gases nitrogen, carbon dioxide and oxygen.² Using the depth of the oxygen absorption feature the thickness of the porous silicon overlayer was estimated to be 10μ . The photocurrent of the diodes was found to be stable under soft x-ray exposure; however, the photoluminescence of the porous silicon was not stable for the diodes tested. We attribute this instability in the photoluminescence to heating in vacuum caused by the manufacturing processes used to produce the diode electrodes.

Figure 1: Photoresponse of the two porous silicon photodiodes as a function of incident energy. The quantum efficiency is in absolute units of electrons detected per soft x-ray photon absorbed. The features have been identified by element and multiple order number.

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EXCITED-STATE PHOTOEMISSION FROM LASER-PUMPED C₆₀ FILMSB. S. Itchkawitz[†], J. P. Long[†], T. Schedel-Niedrig[†], and M. N. Kabler[†][†] Fritz-Haber Institute, Berlin; [‡] NRL

Optical absorption, PES, and inverse PES data for C₆₀ have been qualitatively consistent with quasiparticle band structure calculations. However, there remain quantitative questions concerning the near-band-gap spectra and the extent of relaxation or trapping for valence exciton states. We have used time-resolved, excited-state PES techniques in order to clarify these issues. Clean, 99.99% pure C₆₀ films were sublimed *in situ* onto Au or cleaved GaAs. The films were subsequently excited with 5-ns pulses from a Cu vapor laser while synchronized SR pulses produced photoemission from a small, short lived (< 20 ns) population of excited states in the band gap. The figure shows EDC's taken at ~300 K for SR delays of 0, 4, and 12 ns, and ~100 μ s after the laser pulse. The transient photoemission band in the gap is presenting samples of 10- and 100-nm thicknesses and at temperatures of both 300 and 80 K. We attribute this band to photoemission from excitons trapped by either imperfections or by self trapping. The location of the state (near midgap, 1.1 - 1.2 eV above the valence band maximum) suggests a large electron-hole interaction and a substantial lattice relaxation. Also, the height and average lifetime of the band increase upon lowering temperature to near 80 K, and its apparent width is relatively large. Consistency with most of the existing spectroscopic data for C₆₀ can be obtained by presuming a lattice relaxation of about 0.2 eV in both excited and ground electronic states. The films were gradually damaged photochemically by the laser (~2 mJ/cm² per pulse) at 300 K, but damage was insignificant at 80 K.

RESONANT PHOTOEMISSION SPECTROSCOPY FROM AN EXCITED SURFACE STATE ON GaAs (110)

J. P. Long (NRL), B. S. Itchkawitz (Fritz-Haber Institute, Berlin), and M. N. Kabler (NRL)

Irradiation of the cleaved (110) surface of GaAs with a pulsed Cu vapor laser pumps electrons into a surface-state (SS) minimum at $\bar{X}$ near the conduction band minimum. These short-lived (~1 ns) electrons can be detected via PES using synchronized SR pulses as a probe.¹ We find that when constant initial state (CIS) spectra are measured during the laser pulse with the excited state as the initial state, a resonance appears in the wavelength region of surface core exciton transitions involving the Ga 3d levels. We have also obtained similar spectra in n⁺-doped GaAs without laser pumping, in which case the $\bar{X}$ SS is partially occupied in equilibrium. This resonance has long been known for SS's in the valence band (VB). However, the present excited state consists primarily of dangling bonds (DB) on the Ga, a significant difference. Measurements of the orientation and polarization dependences of the resonance have been made. The figure gives a comparison of CIS spectra for the $\bar{X}$ SS (lower panel, n⁺ sample) and the A5, A_s-derived SS just below the VB maximum (upper panel). For the upper trace in each panel the electric vector of the SR is parallel to the Ga DB, while for the lower traces it is perpendicular. This is equivalent to a 180° rotation about the surface normal; all other conditions are identical. In addition to the Fano-like structure of the main 3d spin-orbit components, there are additional orientation-dependent features whose origin is under investigation.

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X24C

W/Be MULTILAYER COATINGS

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B.W. Murray (Light Metals Technologies)

We are investigating W/Be multilayer coatings for new broad-range, high-resolution, multilayer-coated diffraction grating elements to be used in the X24C grating/crystal monochromator. The goal is to obtain as high a reflectivity as possible over the range from 250 to 1500 eV for multilayer periods of 4 to 6 nm. This energy range covers the difficult carbon K edge region where the performance envelope for all material pairs goes through a minimum and the relatively small multilayer period demands interfaces with very small roughness and interdiffusion so that specular reflectance losses to scattering will be minimized. The best reflectance losses to scattering will be minimized. The best reflectivity for a multilayer with abrupt interfaces would be obtained with vacuum for the more transparent layer. In lieu of that, beryllium has the next best performance with high transparency over our target range. We have examined W/Be multilayer reflectivity losses due to roughness and interdiffusion by measurements over the difficult region of use. The multilayers were sputter deposited by Light Metals Technologies on to sub-Angstrom rms roughness fused silica coupons supplied by General Optics. The Figure shows reflectivities of one of test samples for grazing angles of 14.54 and 20.76 degrees. The calculation was based on our thin film program with Debye-Waller type scattering at each interface, bulk densities, and Henke's optical constants and was forced to a better fit at the larger angle.

X24C

CARBON K EDGE REFLECTANCE OF SELF-ASSEMBLED MONOLAYER PHOTORESISTS

J.C. Rife, T.S. Koloski, J.M. Calvert (NRL),
and W.R. Hunter (SFA Inc.)

We have measured the reflectance near the carbon K edge of benzyl chloride silane self-assembled monolayer (SAM) films formed on silicon, gold, and fused silica surfaces. These SAMs are being considered for photoresists in soft x-ray projection lithography.¹ The silane stalks assemble into a single, uniform monolayer forest with the silicon bonding to oxygen on the surface, the C₆ ring connected just above, and a CH₂Cl group terminating the stalks at the top of the monolayer. Exposure to ultraviolet light or soft x-rays leads to desorption of the chlorine. Lithographic patterns can be formed by chemically selective thick metallization where the chlorine was not desorbed.

Reflectance versus energy was measured in s and p polarization (about 90% linearly polarized) for grazing angles below the critical angle, just above, and at near normal incidence. The figures show the 10 and 80 degree data for samples, 0.7 nm thick, assembled on superpolished silica flats. Monochromator resolution was about 0.25 eV. Least square fits of the reflectance versus angle at each energy yield the monolayer thickness and optical constants.

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NORMAL-INCIDENCE REFLECTANCE OF W/B₄C MULTILAYER MIRRORS IN THE 34-50 Å WAVELENGTH REGION

X24C

J. F. Seely, M. P. Kowalski, J. C. Rife, W. R. Hunter (NRL)

Multilayer mirrors designed to have relatively high normal-incidence reflectance in the water-window wavelength region between the oxygen K absorption edge at 23.3 Å and the carbon K absorption edge at 43.6 Å are important for the microscopy of biological materials. However, such mirrors are difficult to fabricate. Since the period thickness of the multilayer structure is approximately half the design wavelength, the layer thicknesses are of order 10 Å, and the roughness of the interfaces should be small compared to the wavelength (roughness less than 4 Å). The materials must form relatively discrete and stable interfaces. Carbon is a useful spacer (transmissive) layer material for mirrors designed to operate at wavelengths above the carbon K absorption edge, but for wavelengths below the carbon edge the spacer material must have low carbon content. We discuss here the development of W/B₄C multilayer mirrors that have relatively high reflectance in the wavelength region 34-50 Å.

The W/B₄C multilayer structures were fabricated by Ovonic Synthetic Materials using the sputtering technique. Each mirror consisted of 100 W/B₄C periods deposited on a superpolished fused silica or silicon wafer substrate. The ratio of the thickness of the W layers to the period thickness was 0.4.

The reflectance measurements were performed using the reflectometer and monochromator attached to beamline X24C. Results for two mirrors are shown in the Figure for the indicated angles of incidence and for s or p polarized light. The peak normal-incidence reflectances are 2%. Comparisons with calculated reflectances indicated that the period thicknesses and interfacial roughness of these two mirrors were (a) $d=17.54$ Å and $\sigma=3.1$ Å and (b) $d=25.74$ Å and $\sigma=3.7$ Å.

The principal difficulty in fabricating multilayer mirrors for the water-window wavelength region 23.3-43.6 Å is interfacial roughness. If the roughness were reduced to 2 Å, for example, the reflectance would be 4% at a wavelength of 34 Å.

Critical Behavior at the Disordering of the Si(113) (3 × 1) Reconstruction

X25

D. L. Abernathy, R. J. Birgeneau, K. I. Blum, and S. G. J. Mochrie (M.I.T.)

Transformations between the phases of a uniaxial overlayer on a substrate have attracted much attention recently. This is in part because modern theoretical approaches have been successful in understanding the critical behavior of two-dimensional Potts or clock models, which are believed to represent the overlayer. An exception not at present understood theoretically, and therefore of special interest, is the disordering of a 3-fold commensurate (C) solid into an incommensurate (IC) fluid. To guide theory, experimental studies of the disordering of 3-fold C overlayers, such as the the (3 × 1) reconstruction of Si(113), are needed. That was the goal of the present study.

Fig. 1 shows x-ray diffraction profiles versus q_x near the surface (5/3, 1) position for several temperatures. Below $T_c = 959.3$ K, the profile consists of a narrow C peak. The full-width of 0.001 Å⁻¹ indicates that the reconstruction is well-ordered over several thousand Angstroms. Above T_c , the intensity (χ) decreases rapidly, while the peak shifts away from the C position and its width (κ_x) increases. Along y (data not shown), there is also an increase in the peak width (κ_y). The shift (ϵ) reflects the formation of uniaxial discommensurations, so that the surface layer is now IC. The peak broadening indicates that the IC-phase is a fluid.

Fig. 2 shows our results for ϵ , κ_x , κ_y , and χ versus $(T - T_c)/T_c$. Also shown is the intensity in the C-phase (I_0). Each shows power-law behavior with exponents $\beta = 0.63 \pm 0.05$ for ϵ , $\nu_x = 0.65 \pm 0.07$ for κ_x , $\nu_y = 1.05 \pm 0.07$ for κ_y , $\gamma = 1.56 \pm 0.13$ for χ , and $2\beta = 0.23 \pm 0.03$ for I_0 . These results are striking for several reasons. First, we believe that the data presented in Figs. 1 and 2 are among the highest quality measurements to-date of surface critical exponents. Particularly impressive is that the scattering emanates from a high-index Si ($Z=14$) surface. Second, the exponent for κ_x differs from that for κ_y (anisotropic scaling). Such behavior is very unusual. Third, the measured exponents are consistent with the hyperscaling relation $\nu_x + \nu_y = \gamma + 2\beta$. Finally, ϵ/κ_x is constant, as expected for a new *chiral melting* universality class, proposed by D. Huse and M. Fisher.

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The Time Evolution of Incoherent Nuclear Scattering from ^{57}Fe Excited with Synchrotron Radiation

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We report the observation of the time evolution of incoherent resonant scattering from the 14.4 keV level of ^{57}Fe excited with synchrotron radiation (SR). The signal of incoherent scattering is weak we therefore placed the sample inside the detector to collect as much solid angle as possible. A hole was drilled into the detector to avoid the incoming and forward scattered radiation.

Two spectra were measured as shown in Fig.(1). The sample thickness was varied to give the two effective thicknesses as show in the figure. The measured time spectra are described by a model with two components. One component has a significantly enhanced decay rate and is the result of recoilfree excitation. The other component has the natural decay rate for an isolated nucleus and results from excitation with recoil. The decay rate of this second component is independent of the sample thickness. With the significant increase in intensity (more than three orders of magnitude) from undulator sources at next generation SR facilities angle resolved incoherent measurements (time dependent PAC) should be possible. The observation of the recoil component demonstrates the potential of this technique for both Mössbauer and non Mössbauer isotopes.

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Fig.(1) Calculated intensity $I_{inc}(t)$ compared with our experimental data for a foil with an effective thickness of $\chi = 3.4$ in the upper plot and $\chi = 5.6$ in the lower plot.

Temperature Dependence of Nuclear Forward Scattering Using Synchrotron Radiation

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Resonant forward scattering of synchrotron radiation (SR) from ^{57}Fe nuclei has been studied over a temperature range from 8 K to the Curie-temperature at 1043 K. The measured time evolutions show the decrease of the Lamb-Mössbauer factor f and the internal magnetic field H_{int} with increasing temperature.

The data compared to theory are shown in Fig.(1). Two features of the time evolution reflect the two phenomena which occur by increasing the temperature.

One is the decrease of the beat frequency due to a decrease of H_{int} and therefore the magnetic splitting. At the Curie temperature T_c the magnetic field is essentially zero as shown in the last curve in Fig.(1). The second is the envelope of the time evolution, which depends on the effective thickness of the sample. The effective thickness is proportional to the Lamb-Mössbauer factor f , which also decreases with increasing temperature. The f -factor is directly related to the mean square deviation of nucleus from its equilibrium position. Therefore a determination of f as a function of temperature is an excellent tool to check solid state theories. To measure f by using nuclear forward scattering from ^{57}Fe avoids many analysis problems of conventional Mössbauer spectroscopy and is therefore ideal for high precision measurements.

It is interesting to note, that f is not equal to one even though in forward scattering no momentum transfer occurs. The reason for that is that the scattering from Mössbauer nuclei is slow compared to lattice vibrations unlike in the case of charge scattering, where the temperature dependence is described by the Debye-Waller factor and is one at zero momentum transfer.

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Fig.(1) Time evolutions of nuclear forward scattering from an 11 μm thick highly enriched ^{57}Fe sample at different temperatures. The spectra show the decrease of the internal magnetic field resulting in a decrease of the beat frequency with increasing temperature. In addition the change of the envelope reflects the decrease of the Lamb-Mössbauer factor f with increasing temperature.

PRESERVING THE HIGH FINESSE OF X-RAY UNDULATOR BEAMS FROM PERFECT WATER-JET-COOLED DIAMOND MONOCHROMATORS

L.E. Berman (NSLS) and M. Hart (U. Manchester)

In order for perfect crystals to both diffract x-rays efficiently and faithfully preserve the high source brightness, Bragg plane slope errors and dilations induced by the incident power should be considerably smaller than both the Darwin angular width of the Bragg reflection and the photon beam opening angle, typically a few to several arcseconds alike. Traditional silicon and germanium crystal monochromators used at existing insertion device beam lines have already failed in this regard; the problem will worsen by up to a factor of 100 at third-generation beam lines. To solve this problem, we examined the feasibility of using diamond as a high-power-density x-ray monochromator crystal by performing a first test in 1992 using the X25₂ doubly-focussed wiggler white beam, which is capable of providing a 200 W/mm² power density. In that experiment, an isotopically-enriched (100)-oriented diamond crystal wafer showed an integrated thermal distortion of 1 arcsecond, when exposed to a 207 W/mm² power density and aligned to diffract 21.7 keV x-rays from the (400) planes in the Bragg geometry. The crystal was cooled by floating it on a liquid gallium-indium eutectic layer spread over a water-cooled copper block. Difficulty in maintaining the crystal stationary was encountered using this mounting, but of greater importance was the observation that the hot eutectic film sitting under the beam footprint (which served as the dump for the transmitted x-ray power) locally dissolved the diamond and left behind a small pit in the bottom surface. Fortunately the remainder of the crystal was unaffected. To address both of these problems, a new crystal mounting in which the diamond was clamped to a support and directly cooled by a water jet was fabricated, and is shown at right. When this was subjected to a 260 W/mm² power density in a test in 1993, a similar thermal distortion to that seen in the first test was observed. The excellent diamond stability gained from the improved crystal mount allowed a raster pinhole topograph of the diffracted beam to be measured. This is shown below left, and compared with a raster image of the direct white beam focus below right (contours at 25% intervals). The white beam shape and size are preserved by the diamond monochromator. In earlier tests of similarly-designed silicon monochromators, this performance was achieved only when the thermal and mechanical strain fields were adaptively compensated.

This work was supported in part by the DOE, Contract No. DE-AC02-76CH00016.

TEMPERATURE DEPENDENT DIFFUSE SCATTERING FROM $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ SINGLE CRYSTALS.

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T. Hinatsu and S. Uchida (University of Tokyo)
Z. Fisk and P. C. Canfield (Los Alamos Nat. Lab.)

X-ray diffuse scattering from single crystals of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ was studied in the vicinity of several Bragg peaks near the c'-axis as a function of temperature. Two single crystals of La-Sr-Cu-O grown by different methods were examined. Sample A was grown at the University of Tokyo by the floating zone method, and had the composition of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, with T_c of 37 K. The other, Sample B, was grown at the Los Alamos National Laboratory by the flux method, and had the composition of $\text{La}_{1.87}\text{Sr}_{0.13}\text{CuO}_4$, with T_c of 10 K. Our pulsed neutron PDF studies indicated significant oxygen displacements along the c-axis of the tetragonal structure. Since the diffuse scattering intensity is proportional to $(Qu)^2$, where Q is a scattering vector and u is a Fourier transform of the displacement field, the diffuse scattering due to these displacements can be studied with a large Q nearly parallel to c axis. Much of the measurements were made for the diffuse scattering intensities around (0,0,14), (-1,1,14) and (-2,0,14) in the tetragonal indices.

The observed diffuse scattering was strongly anisotropic in the (x,x,z) plane reflecting soft a-axis transverse mode and hard c-axis longitudinal mode. The intensity contour plot is shown in the Fig. 1. The diffuse intensity was nearly isotropic within x-y plane, except that the intensity was stronger in (1,1,0) direction reflecting the softening due to the phase transition. The diffuse intensity in (1,1,0) direction increases linearly with temperature. The temperature dependence of the diffuse intensity near the c'-axis in the (x,0,x) plane shows anomaly decreasing with temperature at low q values, where q is a vector pointing from the Bragg peak (shown in Fig. 2).

Scaling and Growth in 2-D: c(2x2) Pb on Cu(100)

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The kinetics of the two-dimensional Ising model is the focus of a great deal of theoretical and experimental effort. The dynamics of adsorbate monolayers on low-index crystal surfaces provides valuable experimental insight about the fundamental nature of two-dimensional systems. The c(2x2) Pb monolayer structure on Cu(100) is an ideal structural realization of the Ising model with an order-disorder phase transition at 463 K. The kinetics of such a system is of great interest since it falls into the category of a non-conserved order parameter (NCOP) problem. The NCOP problem has been studied theoretically as the 2-D kinetic anti-ferromagnetic Ising model, which predicts power law and self-similar growth.

By combining surface x-ray diffraction techniques, a position sensitive detector and the enhanced flux from the X25 wiggler, we were able to measure the time evolution of the Pb c(2x2) superlattice reflection after a rapid quench to a temperature at which the ordered state exists. With a time resolution of 0.1 sec, we collected high resolution diffraction line-shapes, allowing us to observe the Pb overlayer ordering from domain sizes of 50 Å to 700 Å for over 30 min. After fitting the diffraction profiles, taking into account resolution corrections, we discovered that the system exhibits scaling in growth since a single domain size distribution function fits well at all times. The average domain size, obtained from the fits, follows a power law, $\langle R(t) \rangle = A(T) t^x$, where $A(T)$ is an exponential temperature factor and the critical time exponent $x = 0.5$, agreeing with the theoretical prediction for a NCOP system with a doubly degenerate ground state. The figure on the right shows the average domain size vs. time, with the system following power law growth as early as 1 sec after reaching the final temperature. The circles are the average domain size plotted with the left hand axis, the solid line through the data is a power law fit with $x = 0.5$.

X-RAY SCATTERING STUDY OF THE SURFACE OF LIQUID GALLIUM

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X-ray scattering measurements from the liquid-vapor interface of gallium were performed on a new liquid surface reflectometer designed and constructed for use with the focussed white beam available at wiggler beamline X-25. Using X-rays of wavelength 0.6533 Å, relative reflectivities were obtained at wavevector transfers Q_z as large as 1.5 Å^{-1} for selected incident angles α between 1.5° and 4.5° . Their Q_z dependence seems consistent with a Gaussian surface roughness $\sigma \approx 1.3 \pm 0.2 \text{ Å}$, determined from data collected over a smaller range of Q_z at X-22B in June, 1992¹. While not definitive, the results demonstrate the capability of this instrument to carry out large Q_z measurements on liquid surfaces; and that for liquid gallium, the Q_z -range for measurable specular reflectivities is beyond what was attained in this experiment.

February, 1993 tests of the tilt monochromator and incident arm assembly resolved issues of shielding, the use of optics appropriate to the high beam power density produced by the insertion device, tracking of the downward-tilted beam, and characterization of its intensity profile up- and downstream from the incident arm's defining slit. Further tests of the operation of components downstream, including characterizing beam size and divergence at sample and detector positions, as well as ensuring the reliable movement of the X-25 spectrometer table (supporting the UHV sample chamber, Huber goniometer, and detector arm assembly) required a substantial portion of the July, 1993 run for proper commissioning.

Samples for this run were prepared on Mo substrates instead of SS (stainless steel); Ga₂O₃ removal by Ar ion bombardment of the liquid surface had been observed to increase the Ga/SS contact angle. Glow discharge deposition of Ga onto high-Z substrates should improve wetting properties through the long-range forces which compensate for the small differential in the high surface energies of Ga and the substrate.

However, sample curvature and the presence of oxide islands in the beam footprint resulted in broad reflections with diffuse background levels higher than calculated for off-specular scattering due solely to thermally excited capillary-wave excitations. Scattering from various parts of the sample surface was measured as a function of outgoing angle β , it indicated that only a small region of the surface was sufficiently flat to give a good reflection signal. Assuming that the same area of the sample is responsible for the reflection peak at various α , peak minus background levels around the specular condition (signal), scaled by $h_2/\sin \alpha$ (where h_2 is the incident beam height), have a Q_z dependence consistent with reflectivities calculated for $\sigma \approx 1.3 \pm 0.2 \text{ Å}$ (see Fig. 1).

The theoretical ratio of diffuse to specular signal for the resolution used in the experiment was calculated to be 1.83 at 1.5 Å^{-1} for $\sigma = 1.3 \text{ Å}$, where the specular reflectivity is 1.4×10^{-6} . On this basis, the range of these measurements can be extended to Q_z values of 2.0 Å^{-1} with the existing reflectometer. Measurements to this length scale ($2\pi/Q_z = 3.1 \text{ Å}$) would help settle whether layering due to atomic close-packing near the liquid metal surface actually occurs. Taking definitive reflectivity data on the Ga liquid-vapor interface depends critically on the ability to remove oxides from the entire liquid surface; sample curvature merely complicates but does not preclude the measurement and analysis of specular and diffuse scattering.

Figure 1. Reflection signal (peak minus background) scaled and compared to expected reflectivities for surfaces with Gaussian roughnesses of 0.0 (—), 0.9 (---), and 1.5 Å (— · —); the curves are normalized to pass through the data point at $Q_z = 0.5 \text{ Å}^{-1}$.

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PERFORMANCE OF EUTECTIC-COOLED THIN GERMANIUM WAFERS IN A HIGH-POWER FOCUSED X-RAY BEAM

E. H. Kawamoto and P. S. Pershan (Harvard University), L. E. Berman (NSLS), and M. Deutsch (Bar-Ilan University).

Focused white beam from the 27-pole hybrid wiggler at beamline X-25 provides a total power of 75 W after transmission through a total of 0.75 mm beryllium and 0.17 mm pyrolytic graphite foil, at typical storage ring currents of 230 mA. In a focal spot size of $0.8 \times 0.4 \text{ mm}^2$, the areal power density exceeds 200 W/mm^2 . While this heat loading has been previously studied on eutectic-cooled Si(111) and Si(220) wafers at this beamline¹, its effects on the performance of Ge monochromators were observed during February, 1993 tests. Their larger angular acceptance makes available more flux at a given energy, while its figure of merit κ/α (ratio of thermal conductivity to linear coefficient of thermal expansion) is one-third that of Si, increasing its sensitivity to thermal distortions which degrade the diffracted bandwidth and throughput of the hot monochromator compared with perfect optics. Wafers of thickness $\sim 1.5 \text{ mm}$, cut and polished for symmetric and asymmetric Ge(111) and Ge(220) reflections, were mounted afloat a thin layer of Ga/In eutectic alloy, on the surface of a water-cooled copper block. Double-crystal rocking curves were obtained at Bragg angles corresponding to an energy of 16 keV using symmetric Ge(111) and Ge(220) as analyzers. Low power curves were taken using a 5 mm graphite absorber, which passed about a quarter of the incident power. No substantial difference was noted between rocking curve lineshapes before and after exposure to the full white beam power. Asymmetry angles were 4.5° for Ge(111) and 8.4° for Ge(220), increasing beam footprints by factors of about 3 and 4, respectively. When normalized to ring current and/or attenuation due to filtering, the integrated intensity of the high-power reflection is about 65 percent of that of the low-power reflection except for symmetric Ge(220) (83 percent). Improvement for the asymmetric reflections is not in proportion to the increase in area over which the incident power is spread, since the thermal bump distortion depends on the nonuniformity of the heat load distribution over the entire crystal surface. The 0.15 mrad (31 arcsec) focussing from the mirror best matches the angular acceptance of asymmetric Ge(111), whose relative throughput was the highest measured here, suiting it well for applications requiring high beam fluxes at small bandwidths.

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Kinetics of Sliding Charge Density Waves E. Sweetland, A.C. Finnefrock, K.L. Ringland & J.D. Brock

Cornell University

As a model system for the observation of non-equilibrium statistical physics, we have examined the dynamic properties of the NbSe_3 charge density wave (CDW) conduction requires the presence of phase-slip at the electrical contacts where collective CDW current is turned into normal electronic current. The driving field for this phase slip is a strain field of the CDW phase – the CDW wavefronts are compressed near the positive terminal and expanded near the negative terminal. When the direction of CDW conduction is switched, the strain field must be rearranged accordingly. We have used high resolution x-ray scattering of the Q_1 CDW to measure the time scales for the establishment of a steady state strain field after such a switch. In order to measure only the local CDW periodicity, the x-ray beam was constrained by slits to look at only a small part of the sample. A schematic illustrating the scattering configuration this is shown to the left below. The time scales depend strongly on the impurity concentration of the NbSe_3 varying from less than a millisecond for very pure crystals ($\leq 60 \text{ ppm}$ Tantalum) as shown in the contour plot below to a few seconds for an intentionally doped crystal with approximately 400 ppm Ta.

X-25

Site selective Manganese X-ray fluorescence spectroscopy

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X-ray absorption spectroscopy is commonly used for electronic and molecular structure. Since many important metalloenzymes contain 2 or more atoms of a particular element, an ability to characterize individual sites is an important development. By using the high resolution fluorescence spectrometer with a Johann geometry in a backscattering arrangement, we have successfully shown that for Mn model compounds, the $K\beta_{1,3}$ peak position and $K\beta'$ intensity are dependent on the oxidation state. Therefore, by monitoring specific fluorescence energies, it is possible to perform oxidation state specific absorption and excitation experiments.

On the focused wiggler x-ray beamline x-25, we have done the fluorescence emission spectra for pure Mn(II), pure Mn(IV) and physical mixture of Mn(II) and Mn(IV) as in figure 1. The physical mixture emission spectra is almost the equivalent of the average of two pure samples. Then we performed the XANES study for above three samples as in figure 2. For the Physical mixture of Mn(II) and Mn(IV), the XANES of Mn(II) site and Mn(IV) site show total different features from the shape to the position, which means that the fluorescence excitation spectra can be selective for a particular chemical state, by monitoring the appropriate emission energy of the absorption spectra.

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X26A

SYNCHROTRON XRF EVIDENCE FOR THE SOURCES AND DISTRIBUTION OF METALS IN PORPHYRY COPPER DEPOSITS

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In order to better understand the possible sources and distribution of metals in porphyry copper systems, synchrotron XRF (SXRF) analyses have been conducted on fluid inclusions from several porphyry copper deposits using the SXRF microprobe at the National Synchrotron Light Source at Brookhaven National Laboratory. Results of these analyses lead to the following conclusions concerning the source and temporal and spatial distribution of metals in the porphyry copper deposits:

- All or most of the copper, lead and zinc in the porphyry deposits is transported into the system by the earliest fluids of magmatic origin. Metal contents of the magmatic fluids are generally in the range of several 100 to several 1000 ppm. Any contribution of metals from the wallrocks is minimal at best.
- Depending on the depth of emplacement and the initial water and chlorine contents of the melt, the metals may be transported out of the magma by a low salinity liquid or a vapor phase or by a hypersaline brine exsolving directly from a melt.
- If aqueous fluid immiscibility occurs, the metals are almost quantitatively partitioned into the higher salinity liquid, which coexists with a low salinity, metal-depleted vapor.
- Hydrothermal fluids most closely associated in time and space with economic mineralization have very low metal content between the early magmatic fluids and the later meteoric-dominated fluids associated with mineralization.
- Distal fluids in porphyry copper systems have many of the properties of fluids in the cores of the systems (salinity, temperature, etc.) but are devoid of metals.

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TRACE ELEMENT MICROANALYSIS OF TURTLE SHELLS AS A CHRONICLED INDICATOR OF CONTAMINANT EXPOSURE

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There has been interest in recent years at utilizing indigenous organisms as indicators of environmental contamination. It has been suggested that turtles could potentially be very attractive indicator species of metal contamination because they are extremely long-lived organisms, appear to be relatively tolerant to a range of pollutants, and because their shell is comprised of bone (apatite), which is a well known target organ for a number of transition and heavier elements. Furthermore, turtle shells exhibit growth annuli, within which periodic growth deposition bands (daily during active growth periods) are discernible under a microscope, thus providing the potential to examine historical information on exposure to metal contaminants. We have been examining elemental associations and distributions in sediments surrounding a nuclear reactor fuel and target fabrication facility on the Department of Energys Savannah River Site (SRS), near Aiken, South Carolina, where significant quantities of U and other metals, namely Cu, Cr, and Ni were released to the environment since the start of the facility in the early 1950's.

We have also conducted SXRF analysis on sections of shell samples from turtles (*Trachemys scripta*) collected from a pond within the contaminated site and from control turtles (*T. scripta*) collected in a uncontaminated site. We have found significant concentrations of Ni in the bone samples (shells) of the contaminated turtles, with concentrations ranging from 5-10 (mg/kg) bone tissue in the bulk to 65 (mg/kg) bone tissue in defect zones that were only visible in the contaminated turtle shells. These defect zones appeared as inclusions, approximately 100 to 500 mm in size. In addition to very high Ni concentrations, these inclusions were found to be high in Fe and Cu concentrations relative to either the bulk of the contaminated shell or especially compared to the shell of the control turtle. U was not detectable in any of the shell fragments examined, suggesting that there are significant differences in the bioavailability of Ni and U that may be chemically or physiologically based. Additionally, we have obtained bone (shell) samples from individuals inhabiting a pond receiving effluent from a coal combustion waste (fly ash) lagoon and found concentrations of As and Se, common metalloid contaminants in coal combustion wastes, of between 2 and 35 (mg/kg). These constituents were not detectable in shell samples from the control turtles.

Spatially resolved data on the growth annuli suggest different accumulation/deposition patterns for the contaminant metals and metalloids and for nutrient metal cations, such as Mn and Zn. Mechanisms for these observed patterns are currently being examined.

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INVESTIGATION OF SECONDARY X-RAY FLUORESCENCE DURING MEASUREMENT ON CRYSTAL-MELT CONTACT WITH SYNCHROTRON X-RAY MICROPROBE

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The partitioning of trace elements between calcic amphibole and quenched melt (conc. c. amph./conc. quench melt) has been determined with synchrotron x-ray fluorescence microprobe using established techniques (1). Recent measurements have investigated the role of masking one phase with lead tape (i.e. calcic amphibole or quenched glass) during acquisition to avoid any secondary processes that will may affect measured partition coefficients (e.g. secondary fluorescence; 2).

Measurements were performed on beamline X26A using a Si(Li) energy-dispersive detector at 90° to the incident x-ray beam. Synchrotron ring characteristics were 2.584 GeV and an electron current between 202 and 101 mA. Specimens were excited with white light and the beam size was approximately 10 μm. A 170 μm aluminum filter was used on the detector to suppress the intense K energy fluorescence from the major elements in each phase.

We found that analyzing the same samples with and without lead masking complicated the determination of partition coefficients for Ga, Rb, and Sr. When the mask is used, this can be explained by similar energy levels between the L lines of lead and the K line of the elements cited above (e.g. Pb $L_I = 9.18$ keV, Ga $K_{\alpha} = 9.24$ keV). In fact, lead masking did not allow to discriminate the effects of secondary x-ray fluorescence during analysis. We will reinvestigate possible fluorescence with Mo-shield which lacks any K or L lines that overlap with those of elements that we wish to analyze.

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X26A

UPTAKE AND METABOLISM OF OXYANIONS BY FLOATING AQUATIC PLANTS DETERMINED BY X-RAY FLUORESCENCE MICROPROBE AND MICRO-XANES

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The health and productivity of wetland areas has received much publicity in recent years in regards to these rapidly disappearing habitats for migrating birds. At the Savannah River Site near Aiken, South Carolina, coal combustion waste (fly ash) enriched in heavier metals has been directly deposited from the plant to unlined basins. Runoff from these fly ash basins has led to accumulation of toxic metals in many trophic levels of the food chain in the surrounding wetlands. Knowledge of the bioaccumulation of these metals by floating aquatic plants is severely lacking. Some of these organisms represent the smallest members of the flowering plants, measuring no more than 1-2mm in breadth, which makes metal uptake studies in individuals difficult or impossible. Despite their small size, these plants constitute a significant portion of the bio-mass in wetland areas. SXRF microprobe analysis is an excellent tool to perform in situ measurements of metal accumulation. *Salvinia rotundiflora*, *Wolffia brasiliensis*, *Lemna minor* and *Azolla caroliniana* were investigated for their ability to accumulate trace levels of the oxyanions: selenate, chromate and perchlorate. SXRF measurements showed a thousand-fold increase in Se and Cr concentrations in the tissues of these plants. There was no measurable accumulation of rhenium. Spatially localized measurements indicated a heterogeneous distribution of Se and Cr throughout the tissues but no specific localization in the roots or leaves. Since these metals are not transported from the roots to the leaves in terrestrial plants, we believe that the metal uptake is occurring across all tissues in contact with the water. Micro-XANES was performed on these same plants to investigate changes in the oxidation state of the accumulated Cr and Se. The loss of the pre-edge feature in the Cr XANES spectrum, indicative of Cr(VI), demonstrates the complete reduction of the Cr(VI) to Cr(III) after uptake by the plant. A shift of the Se white-line edge was observed for the Se in the tissues of *S. rotundiflora* as compared to the applied Se. After measuring the Se XANES edge shift using standard mixtures of Se(VI) and Se(IV), we infer the partial reduction of approximately 50% accumulated Se(VI) accumulated in the plant tissue to Se(IV). The information learned from these experiments is important to understanding toxicity hazards in wetland ecosystems, as well as designing potential remediation strategies that use these organisms as bioaccumulators of these toxic metals in these impacted wetland areas.

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X26A

INTEGRATED APPLICATION OF SYNCHROTRON X-RAY FLUORESCENCE SPECTROSCOPY (SXRF) AND EDX IN THE RESEARCH OF COLLOID-FACILITATED CONTAMINANT TRANSPORT

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It has become increasingly evident that mobile colloids may be a primary vector for facilitating the transport of contaminants to and through subsurface environments. A problem in modeling this contaminant transport process has been in defining which mobile phase the contaminants exist in, be it the mobile-aqueous or mobile-solid (colloidal) phase. Integrating results from SXRF generated at X-26A and Energy Dispersive X-Ray Analysis (EDX) provided information about the composition of individual colloids and about the identity of contaminants transported by mobile colloids collected from a contaminated aquifer. A number of contaminants, namely, Cr, Ni, Cu, and Pb were detected by SXRF directly on clusters of mobile colloids collected within a plume downgradient from a decommissioned seepage basin and served as unambiguous signatures of the source term. This provided direct evidence that colloids were active in the transport of these contaminants. Because of poorer sensitivity, EDX did not detect these contaminants but was useful in detecting the abundant and geochemically important elements, Al and Si, that were not measurable by SXRF. This information was combined with XRD and differential scanning calorimetry data and was useful for categorizing the mobile colloids into four primary mineral classes, quartz, kaolinite, hydroxy-interlayered vermiculite and goethite. Additionally, the greater spatial resolution of EDX provided information on elemental composition of individual colloids, as opposed to clusters of colloids. Combining the metal data obtained with SXRF with the elemental data from the EDX suggested that a small percentage, <5%, of the colloids had contaminants on their surfaces and it appeared that the Fe-oxide colloids were especially active in this transport process.

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METAL DISTRIBUTIONS IN IMMISCIBLE FLUIDS: EVIDENCE FROM SYNCHROTRON XRF ANALYSES OF SYNTHETIC FLUID INCLUSIONS

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The metal contents of the synthetic fluid inclusions generated in the $H_2O - NaCl$ two-phase field at 700°C and 700 bars with fO_2 buffered at $Ni - NiO$ and pH buffered at K-M-Q were measured at the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory. The X-ray beam used at NSLS (X26A) has a cross section at the sample surface of about $8 \times 10 \mu m$, permitting analysis of single, pre-selected individual fluid inclusions. The system was calibrated using capillaries of known volume and wall thickness containing solutions of known composition. Results obtained from inclusions were rationed to these calibrants to obtain quantitative analyses of metal concentrations of individual fluid inclusions. In order to test the accuracy and precision of this technique, synthetic fluid inclusions containing known and variable concentrations of $SrCl_2$ were synthesized and analyzed. These fluid inclusions yielded SXRF concentrations within 2-25% of the known composition in all cases. This test also confirmed that the inclusion volume must be known very accurately to obtain meaningful quantitative results.

Metal concentrations of the synthetic fluid inclusions trapped in the two-phase (liquid + vapor) field were determined using SXRF. Vapor-rich inclusions were found to contain 50-150 ppm Cu and Pb, and 1000-2000 ppm Zn. Liquid-rich inclusions contained 3000-9000 ppm Cu and Pb, and 15000-25000 ppm Zn. The results show that Cu and Pb are strongly partitioned into the liquid phase, which consistently contains 100 times the concentration of the metals in the vapor-rich inclusions. Zn is less strongly partitioned into the liquid phase, with concentrations in liquid-rich inclusions typically only 25 times greater than the vapor-rich inclusions.

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SURFACE STRUCTURAL CONTROLS ON TRACE ELEMENT INCORPORATION DURING CRYSTAL GROWTH OF MINERALS

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Synchrotron X-ray fluorescence microanalysis of trace elements in minerals has revealed heterogeneous distributions that correlate to time equivalent portions of symmetrically nonequivalent subsectors (regions of a single crystal, contained within a given sector, that have formed by growth on associated vicinal faces of growth hillocks present on the crystal surface). Such compositional zoning is known as intrasectoral zoning. A wide variety of minerals such as calcite, $CaCO_3$; apatite, $Ca_5(PO_4)_3(F, Cl, OH)$; topaz, Al_2SiO_4F ; and dolomite, $CaMg(CO_3)_2$ have been found to exhibit intrasectoral zoning as well as sectoral zoning. Variations in the concentration of any given trace element may be as large as a factor of 2 to 8 in all of these minerals. The presence of intrasectoral and sectoral zoning exemplifies the importance of surface structure on trace element partitioning during crystal growth.

Differential partitioning in a given mineral is species dependent and is found to varying extents for a large number of cations as well as anions present in trace quantities. This differential partitioning is interpreted to result from structural differences between nonequivalent growth steps and more specifically the geometry and coordination of available protosites within the step comprising vicinal faces of growth hillocks.

Such variations in trace element distribution indicate nonequilibrium partitioning and suggest that there is no unique value of the effective partition coefficient, k_{eff} , for a given mineral-fluid system; rather there are different values of k_{eff} for structurally distinct regions of a crystal surface.

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X26A

DIFFERENTIAL PARTITIONING OF SELENIUM (SELENATE) IN SYNTHETIC CALCITE SINGLE CRYSTALS: EVIDENCE OF SELENATE SUBSTITUTION FOR CARBONATE

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Pristine growth surfaces of calcite single crystals grown at room temperature in aqueous solutions containing SeO_4^{2-} were analyzed for their Se content by SXRFMA using the X-ray fluorescence microprobe operating on beam line X26A at the National Synchrotron Light Source, Brookhaven National Laboratory. The figure shows a typical SXRFMA spectrum of a SeO_4^{2-} -doped calcite crystal. A 19.2 mm Kapton filter inserted between sample and EDS detector strongly attenuated low-energy lines (e.g., Ca $K\alpha$). Peak areas for Se $K\alpha$ and Ca $K\alpha$ X-rays were obtained from a graphical fitting program, and Se concentrations were determined by comparing the peak area ratio of Se $K\alpha$ /Ca $K\alpha$ to that calculated using the NRL X-ray fluorescence program.

SXRFMA of pristine (10 $\bar{1}4$) calcite growth surfaces show that Se concentrations of polygonized subsectors range from 225 to 950 ppm, which corresponds to 407 to 1,720 ppm SeO_4^{2-} . Intrasectoral zoning of these crystals is documented by a 2 to 3-fold difference in Se (SeO_4^{2-}) content between subsectors associated with nonequivalent vicinal faces of growth hillocks on {10 $\bar{1}4$ }. Surface-dependent partitioning of SeO_4^{2-} provides evidence of non-equilibrium trace anion partitioning. The systematic variation can be explained by differences in size and geometry of kink sites in steps on nonequivalent subsectors. The SeO_4^{2-} ion, which is significantly larger than CO_3^{2-} , is preferentially incorporated in the larger and geometrically less constrained kink sites. This positive correlation requires surface-structural (i.e., crystallographic) controls on SeO_4^{2-} incorporation and, therefore, is consistent with SeO_4^{2-} substitution for CO_3^{2-} .

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X26A

INTRA-AGGREGATE SELENIUM CONCENTRATION HETEROGENEITIES: SYNCHROTRON X-RAY FLUORESCENCE MICROPROBE STUDIES OF KESTERSON RESERVOIR SOILS AND LABORATORY SIMULATIONS

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The synchrotron X-ray fluorescence microprobe (SXRFM) at the National Synchrotron Light Source (NSLS) was used to map distributions of selenium and other elements within soil aggregates collected at Kesterson Reservoir, CA, which was previously contaminated with seleniferous agricultural drain waters. 1 mm thick (effectively infinite thickness) sections of intact soil aggregates were scanned on a 0.5 mm grid. Such analyses indicated large variations in Se concentrations within distances of ≈ 1 mm in individual soil aggregates.

The possibility that such heterogeneities were generated by anaerobic microsites within aggregates was investigated via laboratory simulations of Se contamination of individual aggregates. Two-dimensional, discoid, synthetic aggregates of various sizes (1 to 15 mm nominal diameters) and water contents (≈ 50 to 100% saturation) were constructed from previously uncontaminated soils collected from near Kesterson Reservoir. Platinum electrodes were embedded at various points within some aggregates to provide indications of gradients in redox potentials. In some cases, sections of *Scirpus* roots were embedded within aggregates to provide local regions for enhanced microbial activity. After uniformly distributing Se contaminant within each aggregate using 240 (g/m³) solution of selenate [Se(VI)], and flowing 7 to 20 days of incubation, these synthetic soil aggregates were scanned with the NSLS beamline X26A SXRFM to map spatial distributions of Se, Fe, Br, Sr, Pt, and various other elements. Only the samples with embedded root sections displayed substantial heterogeneities in Se concentrations. As much as 40-fold increases in total Se were observed in soils within 1 mm of such organic matter inclusions.

Such heterogeneities probably result from Se reduction to less mobile Se(VI) and insoluble Se(0) in the region of active organic matter decomposition, which in turn induces Se(VI) diffusion towards such zones for further reductive concentration. Future studies of similar systems using a combination of SXRFM and valence-sensitive X-ray absorption spectroscopy will help test this hypothesis. The small-scale variations in total Se suggest that appropriate reference volumes for expressing Se concentrations in soils are sometimes comparably very small, and may also help explain currently observed slow reoxidation of Se in these soils.

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FARADAY ROTATION EFFECT IN HoFe_2

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The angular dependence of the Faraday effect at the $\text{Ho } L_3$ edge was measured at 300 K (room temperature) and at 180 K in a HoFe_2 powder sample. In this experiment a tuneable x-ray polarimeter, set up at the National Synchrotron Light Source at Brookhaven National Laboratory was used. The polarimeter differs from the previous design¹ in the offset mechanism of the polarizer and analyzer crystals. This new design will be described in detail. The quadrupole and dipole contributions to the Faraday effect were compared to results predicted by recent theories^{1,2}. The experimental results do not agree with the predictions but are consistent with magnetic circular dichroism^{3,4} measurements.

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The Biological Efficacy of Auger Electron Emission Using an Indium-labeled Boronated Porphyrin: Photon Activation Therapy

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Photon Activation Therapy (PAT) is a binary system which utilizes a high Z element as a target atom for subsequent activation by monochromatic photons above the K absorption edge of the element. By inducing a photoelectric effect in the atom, Auger electrons are emitted. If the atom is localized to a critical target within a tumor cell, the low energy Auger electrons ionize the critical target and impart a high-LET type, non-repairable damage to the tumor cell. PAT was first proposed by the late Dr. Ralph G. Fairchild of BNL for the treatment of malignant brain tumors using iododeoxyuridine (IdUrd) and samarium-145 radiation sources interstitially implanted in tumor via brachytherapy techniques. The biological efficacy of Auger electron emission for PAT with IdUrd was previously demonstrated using monochromatic photons obtained from beam X17B1.

Preliminary experiments were carried out at beam X27B at the National Synchrotron Light Source (NSLS) using an indium-labeled boronated porphyrin (In-BOPP) incorporated in V-79 Chinese hamster cells. At a dose rate of ~ 0.6 Gy/min, monochromatic photons above (28 keV) and below (27.8 keV) the indium K absorption edge (27.9 keV) were used to test the efficacy of the compound for PAT. A sensitization enhancement ratio (SER) of ~ 2 was obtained for cells irradiated above the indium K edge (see Fig. below; (-) represents below K edge, (+) represents above). Indium incorporation was determined using neutron activation analysis techniques. Measurements indicated uptake of $\sim 10^8$ indium atoms per cell. It is anticipated that the currently available iodine-125 (28 keV) brachytherapy sources will be most suitable for PAT with In-BOPP, and should provide an additional therapeutic advantage of ~ 2 for irradiation at a low dose rate (0.6 Gy/hr).

Performance of X-ray Thin-Film Waveguides and Resonant Beam Couplers

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It has been established recently that x-ray thin-film waveguides are capable of sustaining guided propagation of hard x-rays and 'air-prism' resonant beam couplers (RBC) can function similarly to optical prism couplers.[1] The most important factor that limits the coupling efficiency of a RBC is the photoelectric absorption in the waveguide/RBC structure. By using high energy x-rays ($E > 20$ keV), the effect of photoelectric absorption may be largely eliminated. In this study, we have measured the coupling efficiency of the RBC as a function of the incident photon energy. In a waveguide structure composed of an input RBC, 1 cm guiding section and an output RBC, the intensity of the output x-rays was found to increase by a factor of over a thousand when the photon energy was varied from 12 and 21 keV, reflecting the dramatic reduction in the x-ray attenuation in the guiding section as well as the increase in the coupling efficiency.

One of the most important applications of the RBC is beam compression whereby the coherent flux of a highly collimated and monochromatic x-ray beam can be enhanced significantly, possibly by a factor of 100 to 1000. The highly intense beam must be, however, retrieved not by using an output RBC, but with a scheme shown in Fig. 1. In the near field, the output beam fanning out the waveguide body retains almost the full beam intensity as that inside the waveguide, and thus is instrumental to such possible applications as hard x-ray microscopy. We have measured the far field intensity distribution shown in Fig. 2. Due to mode mixing in the waveguide, the output pattern consisted not only two principal maxima representing the excited mode, but also a series of maxima resulting from a coherent interference of all guided modes existed in the waveguide.

We have also studied the effect of x-ray beam coherence. For optical waveguides and prism beam coupler, a laser beam may be treated as being infinitely coherent; whereas for x-ray beams, the spatial coherence is at most of the order of microns, therefore limiting the total flux available for compression. We have found that for a beam whose size was greater than its spatial coherence length, the coupling efficiency was indeed determined by the coherence length.

Our further efforts in achieving even greater beam compression include making air-gap waveguide to eliminate completely the absorption in the 'film', and fabricating two-dimensional RBC that will allow flux enhancement in both dimensions normal to the x-ray beam.

Fig. 1

Fig. 2

[1] Y.P. Feng, S.K. Sinha, H.W. Deckman, J.B. Hastings, and D.P. Siddons, Phys. Rev. Lett. 71, 537 (1993)

HARD X-RAY (+ 25 KeV) DIFFRACTOMETRY FOR MULTILAYER CHARACTERIZATION*

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A 4 axis diffractometer was set-up on X27C in order to obtain high resolution hard x-ray scattering data from two multilayer samples. The backbone of the system consisted of the 4-circle Huber Diffractometer, with additional placements for the samples. The silicon monochromators and analyzer crystals were channel-cut, double (220)-reflection crystals. The individual crystal geometry allowed for monochromatic reflection of x-rays in the range from 25 to 65 keV. In order to limit the beam spot on the sample, a 20 micron wide slit of 10mm length, positioned immediately before the sample. A fine discrimination window was set around the pulse height from the Ge-Detector.

The samples consisted of one W/C multilayer with 10 identical periods of thickness 39 Å, and a Ni/C multilayer with 500 periods where each layer spacing is different from the previous one ranging from 200 Å to 26 Å (super mirror).

By removing the analyzer crystal and blocking the direct beam we were able to measure the total reflectivity of both samples at 35 keV and 65 keV (see Figure 1 and Figure 2). Scanning the analyzer crystal, the immediate neighborhood of the specular reflection was probed for 35 keV and 65 keV, revealing peak-structures with FWHM's less than 6° and 3° respectively. A number of complete transversal g-scans were performed for both energies. For 65 keV the results were barely distinguishable from background. For 35 keV, very interesting results were obtained for the continuously graded multilayer; a series of intensity dips where the angle of the incoming or reflected beam corresponds exactly to the position of the intensity peaks in the total reflectivity (see Figure 3).

Our tentative conclusion is that, it is possible to perform diffractometry at 25-65 keV, but that the intensity of the beam at 65 keV is not high enough to provide the necessary count rates for extensive diffuse scattering. With this data (and data taken at 8 keV with a traditional anode), we will be able to compare model fits for different energies, and calculate the effective area and point spread function of x-ray telescopes employing the super mirrors. Finally the transversal scans at 35 keV should be thrown into the present discussion on diffuse scattering in multilayers.

1 35 keV total reflectivity measurement of Ni/C Supermirror

2 Measurement of total reflectivity at W/C periodic multilayer at 65 keV

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3 Transverse scan at Ni/C supermirror at $2\theta = 0.34^\circ$

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