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BNL-52131
UC-400
(General Energy Research -
DOE/OSTI-4500-INTERIM 2)

BNL--52131

DE89 000408

National Synchrotron Light Source Annual Report 1987

(For the period of October 1, 1986 through September 30, 1987)

Editors:

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October 1987

**The National Synchrotron Light Source Department
is supported by the
Office of Basic Energy Sciences
United States Department of Energy
Washington, D.C.**

**Brookhaven National Laboratory
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**Under Contract No. DE-AC02-76CH00016 with the
United States Department of Energy**

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Synchrotron radiation is being used at U11 to induce and to study chemical reactions in molecular complexes. In one series of experiments, the energetics reactions involving 1,3-butadiene-SO₂ was elucidated, using a photoionization mass spectrometer. In other experiments, dissociative photoionization processes in Van der Waals dimers and trimers were studied. These processes involve the transfer of atoms from one moiety to another.

The use of visible fluorescence to vibrationally resolve autoionization of core hole resonances was demonstrated by a research team from Boston University for nitrogen. By monitoring the B→X transitions in N₂⁺ it was shown that the cross section for the v'=1 vibrational level increases relative to that of the v'=0 level for resonant core hole excitation compared to photoionization at 50 eV. In other experiments, a research team from the State University of New York and Stony Brook luminescence from O₂⁺⁺ ions was discovered, demonstrating that fluorescence detection will allow characterization of the final state of Auger decay with the high resolution of an optical spectrometer.

A research program on U15 is directed at learning about the chemical consequences of core electron excitation in molecules. The techniques of photoelectron, mass, and fluorescence spectroscopy are being used to reveal how and why unimolecular decay of the core hole varies with molecular structure, and depends upon the nature of the excited state of the core hole. Results for nitrous oxide indicate the importance of molecular orbital atomic populations and overlap populations. A theory, based on the concept of orbital force, is being developed to explain or predict fragmentation patterns of polyatomic molecules following the multiple electron excitation and ionization that accompanies decay of a core hole.

X-ray fluorescence is being used on X24A to probe the properties of atoms and molecules. Progress was made in eliminating well-known problems with this technique and in opening new areas for study. Multiple vacancy effects were revealed, resonance fluorescence (scattering) was shown to avoid lifetime broadening, and energy selective excitation and polarization analysis were used to provide information about the spatial configuration of various orbitals.

X-ray reflectivity, scattering, and induced fluorescence is being used on several beam lines (X22, X18B, X3) to provide structural information about molecular monolayers, films, and interfaces, and about liquid crystals, polymers, polymerization kinetics, sol-gel transitions, and protein dynamics.

David Hanson
Subgroup Representative

X-Ray Crystallography

X-ray crystallographic experiments on powders or single-crystal samples were performed at nine or more beam lines around the X-ray ring during 1987. Additional stations are now being implemented and markedly increased activity in this field is expected in the future. The experimental problems have ranged from diffuse scattering experiments to complete data collections from biological macromolecules. A few areas of research will be exemplified below; powder diffraction studies are covered in a separate summary.

Macromolecules. Complete collection of data using rotation photography techniques in the energy range 8-12 keV were performed at several experimental stations during 1987. The dedicated protein crystallography station X12C was particularly active, and high-resolution data sets to 1.9 Å or better were conveniently obtained in less than two days. A total of well over 135 eight-hour shifts of data-collection time was allocated to protein crystallographic work. Major users were visitors to Brookhaven and the PRTs and groups from NASA, Oxford University, the University of California, MIT, Johns Hopkins, and the University of Pittsburgh.

Microcrystals. The high intensity of monochromatic X-rays was used to collect intensity data from microcrystals too small to be studied by conventional X-ray sources. Interest was focused on studies of catalytically important zeolite crystals, and initial studies of crystals in the 10 μm diameter range verify the potential for single-crystal studies of crystals down to a few μm on edge. Groups from Exxon (X10A), the BNL Chemistry Department and Mobil (X13B) developed microcrystal diffraction techniques for future use.

Multiple Scattering. Multiple scattering techniques were employed in pilot experiments aimed at the direct-phase determination of crystallographic structure. The excellent collimation and tunability of the radiation to long wavelengths allowed direct observation of phases in systems such as Si and Ge₃₈As₈I₈ [Polytechnic University of New York, BNL Chemistry Department (X13B)] and V₃Si and benzil [Purdue University (X18A)].

Diffuse Scattering. An important area of research was the use of diffuse scattering, notably on the Oak Ridge X14A and on the SUNY X21 beam lines. The study of the material Ni(75+x)Fe(25-x) around the different absorption edges revealed surprising differences in size of the two different atoms in the crystal lattice. Other interesting studies include

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SECTION 1

INTRODUCTION BY THE CHAIRMAN

Last year was a busy and productive year at the NSLS. The Users and the staff were all serving multiple duties: building and commissioning the rings and the beam lines; operating the facility and conducting scientific programs; installing upgrades and Phase II insertion device capabilities; and expanding the building. All this activity stretched us a little, but we saw improvements in the performance and understanding of the storage rings, and the establishment of an extremely broad and productive beam line inventory and experimental program. We made an aggressive step into the next generation of capabilities with installation of a full spectrum of insertion devices on our high brightness storage rings. Next year, 1988, will find us with over 90 experimental stations on the two storage rings, and a dozen insertion device stations on seven insertion devices. We worked hard to bring the storage rings as near as possible to their "final" configurations in coincidence with the Phase II installation, so that we will have uninterrupted operations well into the future. The unprecedented size and breadth of the capabilities of the NSLS, the number and complexity of the institutional and disciplinary involvements and commitments, and the size of the User community we seek to serve will provide us with scientific and management challenges for many years.

Priorities, Policies and Procedures

The various groups which provide advice and counsel to the NSLS management and the User community have been active this year.

The Program Advisory Committee (PAC, see Table 1) dealt with the allocation of the resources of the bending magnet and insertion devices with the approval of five new Insertion Device Teams and four new Participating Research Teams. The Advisory Committee continually examines the philosophy and methodology that is evolving to deal with the crush of Users and equipment that we have, and help the management of the NSLS and Users set priorities for the allocation of resources.

Over the past year the Users Executive Committee (UEC, see Table 2) provided a clear picture of the needs of the User community. The UEC subcommittees on housing, space, parameters, laboratories, and scheduling had an important impact on NSLS priorities and operating procedures, and pointed the way for needed changes in many areas.

The General User Oversight Committee (see Table 3) took on the job of assuring that the beam time available to the "General User" is efficiently and equitably allocated, and that, ultimately, the best science gets done. The General User program at the NSLS is critical in fostering wide involvement by the scientific community and in providing open access to all NSLS resources.

The PRT/IDT Council is made up of the principal investigators of the PRTs and IDTs and provides a direct link between NSLS management and the management of these important partners in the facility (see Informational Guides in User Administration section). The Council will provide a forum for the PRT/IDT community to establish its agenda and to provide advice and guidance to the NSLS in setting the policy and priorities dealing with the PRTs and IDTs, and in establishing our long-term goals and priorities. The Council is in its formative stages, but promises to develop a strong voice commensurate with its importance at the NSLS.

Finally, we recently formed The Scientific Program Support Committee (Table 3) which has the charge of taking a broad look at the operations of the facility to define ways in which the NSLS can be better and more smoothly utilized. They will identify any existing problems and weaknesses and find ways to deal with them. One lesson we have learned is that the system must be open, communications must be good, and people must work together.

Phase II Shutdowns

The shutdowns of the VUV and X-ray Rings for upgrades and installation of Phase II insertion devices and beam lines are well along, but have not been without problems. The VUV shutdown went close to schedule and included the installation of an Infrared beam line, the Transverse Optical Klystron (TOK), and provision for a spectroscopy beam line utilizing the TOK wiggler. New power supplies and a revamped RF system, together with an improved operating configuration, led to improved stability and reliability. The VUV ring now is in full, routine operations, and has two functioning insertion devices.

The X-ray shutdown is a more demanding project. The installation of new injection hardware and the Laser Electron Gamma Spectroscopy (LEGS) project went well and both were successfully commissioned. Subsequent problems with the new insertion device chambers were a serious setback, which cost us a few months, and moved our date for recommissioning from November 1987 to March 1988. The new power supplies were installed and successfully tested and the RF cavities were upgraded. A total of 22 insertion device and bending magnet beam lines are being added as part of the shutdown. Reestablishing the X-ray experimental program will be the first priority of the NSLS for FY 1988.

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9/87

Science at the NSLS

This report contains summary discussions of the scientific areas represented by the Users Executive Committee Subgroups, and individual reports by the Users, arranged by beam line. Throughout the past year many advances were made in capabilities and significant results were obtained. Some examples of particular note are the following.

Imaging techniques are among those which take greatest advantage of the high brightness of the NSLS storage rings. Imaging efforts at the NSLS include soft X-ray microscopy and holography, microtomography, microprobe, microbeam analysis, lithography, topography, and angiography. The X-ray microscopy and holography effort at U15 was given a gain of over two orders of magnitude in coherent power when it moved to the test beamline miniundulator at X17T. New zone plates allowed experimenters to push microscope resolution to the 75 nm range, and Gabor holograms demonstrated transverse resolution better than 40 nm, an order of magnitude improvement over previous results. The X-ray microscopy and holography effort will now move to the full undulator at X1. Microtomography was carried out at X10, X14, X23, and X26. The X10 group employed sophisticated phosphors and CCD detectors, coupled with impressive data reduction codes to push resolution to better than 2.5 microns, with the promise of 1 micron in the near future. Exxon is building a new beam line dedicated to microtomography based on these results. High intensity microbeams at X10, X13, X14, and X26 pushed single-crystal diffraction studies to crystals of the order of 10 microns, and microprobe resolutions to less than 25 microns with ppm sensitivities, opening many new areas of study. Topography, using both white and monochromatic beams at X19 and X23 showed high contrast and strain sensitivity down to 25 micron resolution. The X-ray lithography program at the IBM U6 line has been successful to the point that IBM has purchased a synchrotron to be dedicated to manufacturing development, and IBM was approved by the PAC for the installation of a second lithography beam line on the VUV ring. Soon to be brought on line will be the Coronary Angiography program on the X17 superconducting wiggler beam line.

Soft X-ray science saw some important advances in coincidence studies, spin-resolved spectroscopy, photon-stimulated desorption, molecular dissociation and excitation, and electronic structure of clusters and high-temperature superconducting materials. Measurements of electron-ion coincidence on the X17T spectroscopy line directly linked Auger final states and specific fragmentation events. Electron-electron coincidence measurements on U12 allowed state specific Auger and photoemission measurements on surfaces. The spin-resolved photoemission beam line on the U5 undulator demonstrated spin-sensitive photoemission results for magnetic overlayers. Photon-stimulated desorption work on U8 and U1 demonstrated state-specific desorption on surfaces and also that state-specific chemical and structural information can be obtained. State-selective core level excitations are being employed on U15 to understand Auger-induced fragmentation. At U1, Fluorescence Yield Near Edge Spectroscopy was used to study surface chemistry in a high pressure environment, opening a new area for in-situ research on surface chemistry. Work at U7 on matrix-isolated clusters shows that coupling of the cluster to a surface is critical to its chemistry and can be precisely controlled with rare gas adlayers. U9A has coupled lasers and synchrotron radiation to study photoionization of laser excited atoms. Numerous beam lines were used to study electronic structure and chemistry of high temperature superconductors. The new "Dragon" spherical element monochromator on (SEM) U4B produced a resolving power of better than 1000 and a high angular acceptance, and appears to be the instrument of choice in the soft X-ray region. Three additional SEMs are in various stages of construction or design.

Scattering measurements at X20 and X14 on quasicrystalline materials showed that symmetric peak shifts are associated with a linear phason strain, rather than with Paulings icosatwin model. Diffuse scattering measurements at X14 used anomalous dispersion to highlight size differences and short range order in crystalline FeNi alloys, information that will be valuable in many important materials.

Time-resolved scattering was used to observe hot phonons in quartz (X18), protein unfolding (X21), and crystallization behavior (X21). Surface scattering is now widely used to study surface ordering, melting and roughening, adlayer and adsorbate structure, and liquid crystals. Particularly important work on surface roughening has come out of X10, X16B, and X20. Magnetic scattering has gone from a hope a couple of years ago, to an important and rapidly growing area. Work at X22, X20, and X16 looked at several rare earths, critical scattering in MnF_2 , and separation of orbit and spin in holmium, respectively. An exciting step toward a new generation of scattering was accomplished in the study of nuclear Bragg scattering from nearly perfect $^{57}\text{Fe}_2\text{O}_3$ crystals using an ultra high resolution (5 meV) 4 crystal premonochromator on X12A.

We are seeing greater use of lasers as pumps for time-resolved measurements such as the work at U9 (photoionization), X18 (hot phonons), X24 (electron-hole plasma on Si), and X14 (laser melting of Si). Many more such experiments are planned and several substantial laser installations are being made.

Finally, X-ray absorption measurements, which have formed the bedrock of synchrotron X-ray science since its inception, are being used at two dozen experimental stations around the facility. Current efforts are focused on examining buried interfaces using glancing angle techniques, and a variety of in-situ measurements of chemical and electrochemical systems. Recent advances in the understanding of near edge X-ray absorption fine structure made NEXAFS a widely used surface technique.

Compact Synchrotron For Lithography

The NSLS progressed in its program to assist U. S. industry in the manufacture of high density chips, using X-ray lithography. At a meeting held November 17-18, 1986 (see BNL Report 52046) a detailed plan was drafted which described a project totalling \$394.8 million, broken into five areas.

1. Build an X-ray source within 30 months.
2. Start R&D design and build a superconducting source.
3. Provide a controlled environment building for semiconductor processing.
4. Develop masks and aligners for lithography.
5. Start R&D to demonstrate 0.25 micron resolution, and leading-edge dynamic random access memory.

Funding was received in April 1987 which enabled a program to be started whose first mandate was to prepare a conceptual design report involving the first three items.

Working with BNL's Technology Transfer Office, a fourth workshop was held on July 8, 1987 to develop plans for transferring X-ray lithography synchrotron (XLS) technology to industry (see BNL 52096). It is important to involve industry in the construction phase so that the technology base is developed there as early as possible.

X-Ray Microscopy Symposium

The Light Source was a co-sponsor of the Second International Symposium on X-ray Microscopy at Brookhaven from August 31 to September 4, 1987. Approximately 100 persons from eight countries participated and about 80 papers were presented. This represented a substantial growth over previous symposia on the subject held in 1979 in New York and 1983 in Göttingen.

The symposium was sponsored by the NSLS, The Center for X-ray Optics at Lawrence Berkeley Laboratory, the Stony Brook Physics Department, and the National Science Foundation. The proceedings of the symposium will be published by Springer early in 1988.

Progress in Fresnel zone plate fabrication was reported by several researchers who indicated that resolution in imaging microscopes may be improved to 20 nm in the next several years. Scanning microscopes with zone-plate optics and high brightness synchrotron radiation sources are operating at the NSLS, Daresbury, and BESSY.

Phase contrast imaging microscopy was recently demonstrated by the Göttingen microscopy group.

Source development has been rapid with soft X-ray undulators that now illuminate the microscopes at the NSLS, Daresbury, and the Photon Factory. The high coherent power available from the NSLS "mini-undulator" made it possible to obtain and reconstruct holograms of biological specimens with about 40 nm resolution.

Applications were extensively reported in biological and materials sciences. Contact microradiography is the most frequently used technique, but results were presented from high-sensitivity fluorescent imaging and three-dimensional tomographic imaging that are used at the Light Source.

Michael Knotek
Chairman

SUBGROUP REPORTS

The NSLS Users Organization provides for organized discussions among users of the NSLS facility as well as between the user community and the laboratory administration. Working in concert with this group are nine Subgroup Representatives representing different disciplines at the Light Source. The past and present Subgroup Representatives are listed below. Subgroup reports providing an overview of the science in these disciplines during the past year are also included below.

Subgroup	Past Representative	Present Representative
X-ray Fluorescence	Mark Rivers	Mark Rivers
Lithography/Microscopy	Jerry Silverman	Chris Buckley
Atomic & Molecular Science	David Hanson	David Hanson
X-ray Crystallography	Ake Kvick	Hubert King
X-ray Scattering	Gerald Liedl	Gerald Liedl
Topography	John Billelo	Masao Kuriyama
EXAFS	Pedro Montano	Pedro Montano
Energy Dispersives		
Diffraction	Michael Bennett	Michael Bennett
UV Photoemission & Surface Science	Peter Johnson	Thor Rhodin

X-Ray Fluorescence

The Fluorescence Analysis Subgroup worked exclusively on beam line X26C during FY 1987. The members of the subgroup represent three disciplines: 1) analytical technique development, 2) biomedical applications, and 3) geochemical and cosmochemical applications.

Analytical Technique Development. The X26C fluorescence microprobe was commissioned in April 1986, and was in constant use during FY 1987. It consists of a white light beam line with adjustable slits 20m from the source, a Si(Li) detector, X-Y-Z sample stage, visible light microscope and multichannel analyzer. Spot sizes as small as 25 microns and detection limits below 1 ppm have been achieved in biomedical and geochemical specimens.

Developments in software and hardware allowed the collection of 2-D trace element scanning images. Images with 10 ppm elemental sensitivity and 30 micron spatial resolution were made for both geological and biomedical samples.

A microprobe which uses multilayer Kirkpatrick-Baez optics was tested on the beam line in collaboration with visitors from the Lawrence Berkeley Laboratory. This microprobe achieved a spot size of 10 microns at 10 keV with a bandwidth of 1 keV.

One advantage of using synchrotron radiation for X-ray fluorescence is that the polarization of the incident beam can be used to reduce the background in the fluorescence spectra. This reduction then translates into improved minimum detectable limits (MDLs). However, alignment of the detector-sample-beam then becomes more crucial than in conventional XRF measurements. We developed procedures for rapid alignment of the sample within the beam and for the angle between the incident beam and the detector. The backgrounds are measurably higher (because of poorer polarization) if the sample is more than 10 micro-radians from the vertical center of the beam. It is likely that the vertical beam position is fluctuating more than this, so potentially the MDL may be improved by installing a beam position feedback on X26.

One of the main goals of the fluorescence microprobe is to obtain quantitative analyses in the absence of standards which are very similar to the unknowns. We now can measure the concentration of trace elements using a single major element as an internal standard. The accuracy of the technique generally is better than $\pm 20\%$.

Cosmochemistry. Analyses of trace elements using synchrotron-induced X-ray emission were obtained on a variety of extraterrestrial materials including iron meteorites, micrometeorites from the stratosphere, ablation spheres from Greenland melt lakes and deep-sea sediments, lunar rocks, and refractory inclusions from carbonaceous chondrites. The most significant finding was the observation of Cu distribution coefficients (Cu in troilite/Cu in metal) less than 1 for Ni-rich iron meteorites suggesting that subsolidus re-equilibration was an important process in producing the trace element groupings. Stratospheric micrometeorites (about 10 micrometers in size) showed compositions near those of carbonaceous meteorites for most detected elements but were greatly enriched in Br by factors of 8 to 37. Since Br is detrimental to the Earth's ozone layer, the high content in these particles may have important implications to atmospheric chemistry. The trace-element signatures of meteoritic ablation spheres (about 100 micrometers in size) extracted mechanically from Greenland melt-lakes and magnetically from deep-sea sediments were depleted relative to carbonaceous meteorites for all detected elements with the exception of Pb, suggesting that ablation/melting significantly modified the chemical composi-

tion of the parent material. Compositional clustering observed for the deep-sea particles may be useful in identifying the parental objects. Analyses on igneous meteorites and lunar rocks show that Ba, Ti, and Sr contents and the element ratios Sr/Ba and Fe/Mn are useful parental fingerprints. Sr/Ba was distinct for plagioclase from each of the meteorite and lunar samples. The initial research on refractory inclusions from primitive meteorites determined the melilite/liquid partition coefficients for refractory lithophiles in synthetic melts, which were between 0.2 and 0.1 for three rare earth elements (Sm, Y, and Yb), unity for Sr, and less than .002 for Zr. The values for rare earth elements are slightly less than rough estimates based on neutron activation analyses of mineral separates.

Geochemistry. The X-ray fluorescence microprobe enables geochemists to study concentrations of the elements of individual minerals, or within a single mineral grain. A variety of projects were carried out on the X26C beam line. Two representative studies were:

1. Concentrations of precious metals in common sulphide materials. These studies are important economically and also important for the information they provide on processes of ore deposition.
2. The diffusion rates of trace elements in rhyolite glasses was measured by comparing the concentration element profiles at 10 micron intervals across the interface between two glasses of different composition after they had been in contact at high temperature and pressure for different times. The results suggest that the trace element diffusion is strongly controlled by the major elements, with rates much lower than "tracer diffusion" studies would suggest.

Biomedical. Experiments were conducted to develop thin target standards within a biological matrix, refine methods for preparing specimens for SRIXE analysis, and to characterize the distribution of various trace elements in brain, liver, kidney, and bone.

Gelatin solutions containing trace elements of biological interest were frozen, cryosectioned at 20 μm , and freeze-dried to make thin standards of known low Z matrix. This approach circumvented the necessity of extrapolating from thick Standard Reference Materials to thin unknowns.

Several biological experiments were done by PRT members and by outside users of the X26 beam line: these fall under three general categories:

1. Distribution of essential trace elements: The microscopic distributions of K, Ca, Cu, Fe, Zn, and Br were evaluated in biological structures which were too small or too complex in shape to dissect for conventional chemical analyses. The organs or tissues examined included cerebrum, cerebellum, kidney, and liver. The trace element content of the microscopic structure is correlated with the biochemical function of the elements in that structure.
2. Localization of toxic elements: Understanding the microscopic distribution of toxic metals is important to provide better indices of exposure and toxicity. Experiments measured and related the microscopic distribution of lead in bone and cerebrum to the metabolism and toxicity of lead in these tissues.
3. Localization of metal-containing drugs: Several drugs contain metals such as Pt, Cu, and Fe. Experiments were conducted to investigate the localization of the metal moiety of two antitumor drugs, cis-platin and gallium nitrate, in normal and tumorous tissue. The localization of these drugs in the target cell is important to optimize dose for delivery of the drugs, and to evaluate the potential for improved drug delivery with different derivatives of the drug.

Mark L. Rivers
Subgroup Representative

Lithography/Microscopy

The past year was marked by continuing advances in X-ray lithography and new developments for soft X-ray microscopy and holography.

In lithography, the IBM group working at U6 continued its work in several areas. The size of the group increased significantly, as researchers from the IBM East Fishkill manufacturing site joined those from IBM Research.

Radiation damage to the thin membranes used for mask substrates recently received a lot of attention. It was learned that boron nitride membranes, once considered a leading material for such substrates, are susceptible to radiation damage which may cause distortion that is unacceptable for high-resolution lithography. Studies were performed to learn more about the mechanism of damage and its dependence on other properties of the material. Since the membranes can be made under a variety of conditions, which permits the tailoring of some of their properties, such experiments may be useful in determining what other materials are less sensitive to radiation damage.

The IBM stepper was used to learn more about making working devices using X-ray lithography. The stepper was modified and upgraded; it is heavily used for experiments in device-making, with studies underway to determine overlay and linewidth control capability. A significant effort went into developing a resist technology with the resolution and linewidth control necessary to make sub-micron devices. Meanwhile, work is in progress to develop new resist systems for future use, with the goal of finding ones with better sensitivity, in addition to improved characteristics of resolution and linewidth. A group from Rensselaer Polytechnic Institute continued their study of the exposure chemistry of resists, working primarily with PMMA.

Perhaps the most significant and exciting news came in June when it was announced that IBM contracted with Oxford Instruments to purchase a compact, superconducting storage ring to be installed in East Fishkill for X-ray lithography. The encouraging work done at beam line U6 at the NSLS over the last several years was an important consideration in reaching this decision.

It also has been a particularly exciting year for microscopy. As part of Phase II, beam line X1A has been designed to use an undulator for soft X-ray imaging experiments, primarily of biological objects. The beam line will be the world's brightest continuous source of soft X-rays and thus will produce the highest, spatially coherent, soft X-ray power. This coherent power is necessary for imaging modes such as X-ray holography and scanning transmission X-ray microscopy.

The installation of a mini-undulator as a test bed on beam line X17T was a major advance. The undulator for beam line X1 will be a 37-period device (now being fabricated). Since it was considered very important to test high-brightness sources before the full Phase II installation, the Light Source installed a ten-period soft X-ray undulator in the existing straight section which illuminates beam line X17. This test bed was operational for nine months. Three experiments were run on the beam line: undulator characterization, scanning microscopy, and holography.

Undulator characterization studies measured the absolute spectral intensity of the device. The results agreed well with theory and indicated an increase in brightness of two orders of magnitude compared to a bending magnet source on the VUV ring, where previous scanning microscopy and holography experiments were done. Operation of the undulator did not interfere with normal operations of the X-ray ring.

The scanning X-ray microscope benefitted from the increased throughput. Images that took over 30 minutes at beam line U15 were made in less than a minute. Microscope hardware and software were rebuilt to allow for the higher throughput. The collaboration of the Center for X-ray Optics and IBM on the manufacture of high resolution zone plates continued, and with the aid of the latest generation of zone plates, a resolution of 75 nm was measured. Images of biological specimens in their natural environment were made. In particular, a collaboration with the Center for X-ray Optics and University of California at San Francisco, provided images of the internal structure of wet, unstained, unfixed zymogen granules from the pancreas of a rat. Such structures are extremely hard to see by any other technique.

Gabor holograms of these zymogen granules were also made possible by the increased coherent flux of the beam line. Holograms of many biological specimens were exposed in PMMA resist, then read out in a transmission electron microscope and digitized. Computer reconstructions of these holograms demonstrated a transverse resolution of better than 40 nm, an increase of over an order of magnitude from the best holograms obtained previously.

The microscopy and holography programs made good progress in 1986 and 1987 toward their goal of high resolution (about 10 nm) imaging of natural, perhaps living, biological specimens.

Jerome Silverman
Past Subgroup
Representative

Atomic and Molecular Science: A Partial Overview

A study of molecular reaction dynamics involving mixtures of rare gases and halogen-containing molecules activated by VUV light was conducted on U9A by scientists from LANL: the motivation is the current interest in high power excimer lasers.

Cross sections of ground and excited-state atomic photoionization are being determined on U9A. This research uses a laser source to prepare a high concentration of excited state atoms, and the synchrotron source to provide the tunable radiation for making cross-sectional measurements over a wide range of wavelengths.

The VUV circular-dichroism studies of nucleic acids are being conducted in U9B to determine the origin of the large positive CD bands around 185 nm. Base pairing rather than the base sequence appears to be important.

experiments on Al-Mn quasicrystals, Ni on sapphire surfaces, KMgF_3 at several temperatures, and the modulated phase of TTF-TCNQ at 15 K.

Electric-field Experiments. Experiments performed at beam line X13B looked at the structural changes as a function of high-voltage external electric field in technically important materials. The high resolution enabled very small changes in the unit cell to be studied as a function of the applied field, and changes in the Bragg intensities between + and - polarization make detailed studies of the atomic and electronic redistribution possible. Materials such as lithium niobate, potassium titanyl phosphate and 2-methyl-4-nitroaniline were investigated by researchers from the BNL Chemistry Department, SUNY at Buffalo, University of Lund, and the University of California. These experiments of structure modulation promise to open up a new area of crystallographic research at the synchrotron.

Åke Kvick
Past Subgroup
Representative

X-Ray Scattering

Since 1985 when the first X-ray scattering experiment was performed at the NSLS, the X-ray scattering community at NSLS has been a growing and dynamic group. In the past year more beam lines designed around scattering capabilities became operational, with additional beam lines coming under development for operations after the X-ray Phase II shut down. Upon completion of the new scattering beam lines, the full set of capabilities for X-ray scattering at the NSLS will be unparalleled. In the early stages of operations, a significant amount of effort went into the development of projects for these beam lines. Problems with the beam line and instability of the source have been a factor. However, in spite of these problems and the short operational period of the X-ray ring this year (Phase II shutdown started in March 1987), a wide range of experiments were conducted. Short summaries of these experiments are given elsewhere in this report.

The spectrum of experiments covers a wide range of X-ray scattering techniques and illustrates the capabilities of the scattering lines at the NSLS. The techniques encompass wide-angle scattering, small-angle scattering, high and low Q-resolution scattering, diffuse scattering, magnetic scattering, time-resolved scattering, and surface scattering. The experiments focussed on all types of phenomena in liquids, monolayers, thin films, artificial superlattices, polymers, ceramics, and metals.

Surface scattering is one class of experiments which utilizes the full range of the synchrotron source. Eight beam lines (X15A, X16A, X16B, X18A, X20A, X20C, X21B, and X22C) were used for this new and exciting technique. (One should note that some of these beam lines are changing to new ports as part of the Phase II effort). The work of researchers from MIT and IBM on X20A and C illustrates the surface scattering work. In one experiment, they clarified the phase diagram of high density xenon-on-graphite to elucidate the essential features of this model system. Their results show that over a broad range of coverage that xenon exhibits a sequence of structures with decreasing temperature. Other experiments on these beam lines include the study of the structure and transition of hydrogen on tungsten, as well as an investigation of a liquid crystal system with a tuneable dimensionality. Other surface studies made use of the X-ray Standing Wave technique, the work by the AT&T Bell Laboratories group on X15A being an excellent example. This investigation considered monolayers of As on Si(100) and found the results in good agreement with a model of symmetric As dimers on the surface. This small example of the surface studies conducted at the NSLS during the past year illustrates the powerful capabilities to undertake studies not previously possible.

Another area where the source characteristics are of critical importance is magnetic X-ray scattering. The new phenomena observed using X22B for the determination of the magnetic structure of erbium (including the discovery of three ferrimagnetic phases) is an outstanding example of how magnetic X-ray scattering can be utilized. The rapid progress in the study of magnetic structures also was shown by the BNL-IBM-MIT collaboration on the study of MnF_2 .

An emerging area is time-resolved X-ray scattering experiments that are made possible by the high flux and timing of the source. A recent experiment by NSLS researchers utilized the time-resolving data acquisition of X18A to study hot photons in quartz arising from a laser pulse. A feasibility study also was recently completed on X21B by researchers from the State University of New York on protein folding. Further, time-resolved small angle scattering was shown to be a real asset. Recent work also by researchers from the State University of New York on X21B illustrated the unique information that could be obtained on a study of crystallization behavior of blends of high and low density polyethylene.

Another aspect of X-ray scattering at the NSLS is the multitude of studies involving diffuse scattering. A group from Oak Ridge National Laboratory (X14) conducted some interesting work on cobalt precipitates in copper, while another group from Northwestern (X18) used diffuse scattering to understand aspects of the precipitation in Cu-Be and Al-Zn alloys.

Finally, the explosion of effort on high T_c superconductors has used the unique characteristics of the source. The work of researchers from the University of Houston on X22 observed a spontaneous monoclinic distortion that may be relevant to the superconducting properties.

These studies provide a brief summary of the many exciting new techniques and experiments that have been conducted at the NSLS. The X-ray scattering community at the NSLS has shown its enormous potential and we look forward to the expansion of this effort with the completion of the Phase II construction.

Gerald L. Liedl
Subgroup Representative

Topography

Introduction. The following are brief summaries of major experiments performed at the synchrotron topography station, on beam line X19C at the NSLS. They were mainly performed on the white beam camera, although the capability for monochromatic topography is also available. The capability for dedicated white beam topography is unique in the United States.

An Experimental Study of the Critical Factors Controlling the Mechanical Properties of Molybdenum and of the Interaction of Interstitials with Body-Centered-Cubic Transition Metals. This work encompassed the theoretical and experimental development of a new high-sensitivity method for the determination of strain fields in perfect to highly deformed crystals with a strain sensitivity of one part in 10^4 and a spatial resolution of 25 micrometers. The technique was implemented by studies of the strain field in the proximity of a stress raiser in Mo single crystals. Variations in the lattice spacing as high as 300% and angular misalignments of 100% over 25 micrometers from a cracktip were detected.

A Theoretical Study of the Critical Factors Controlling the Mechanical Properties of Molybdenum and of the Interaction of Interstitials with Body-Centered-Cubic Transition Metals. This work introduces a modification in the Finnis-Sinclair potentials as a guide to interpreting strain field measurements in synchrotron X-ray topography, with special reference to interactions of interstitials and vacancies. With this modification, good results are obtained for the energetics of instability. Excellent agreement also is found between the lattice parameter dependence of the cohesive energy of Mo as obtained using the modified potentials and via calculations of self-consistent augmented-spherical-waves.

Beam-Line Development for Topography, Tomography, and Microradiography on a Seven GeV Synchrotron Source. Preliminary studies of special interest are focused on those problems where deep penetration of the radiation, energy tunability over a broad range, and/or high speed real-time experiments are essential. To cite a few examples: studies of voids in sintered ceramics, void formation in the bulk during high-temperature creep, dynamics of plastic flow, high resolution strain studies in thin-film integrated circuits, and in situ studies of crystal growth. Design factors necessary for constructing an optimum beam line to effectively utilize 7 GeV radiation, from both the cost and scientific perspective, are in progress. X19C at the NSLS and the white beam station at SSRL will be used as a test bed for carrying out ideas to be incorporated in the proposed new synchrotron facilities.

White Beam Fractography of Mo and Nb Crystals. There were several experimental and theoretical studies using white beam techniques for assessing the fracture behavior of Mo and Nb crystals. Factors of interest included the size of the plastic relaxed zone, the dislocation density, and the interpretation of the image contrast.

Synchrotron X-Ray Topography Observations of Fatigue and Fracture Behavior in Zinc Bicrystals. Crack propagation at 77 K and 298 K was studied for low-cycle prefatigued zinc bicrystals. Synchrotron X-ray Fractography (SXRF) and monochromatic Bragg Angle Strain Contour Mapping (BACM) were used to examine the strain field of the crack in relation to the bicrystal boundary plane. The BACM method has been developed as a powerful tool to study in detail the strain field of a relaxed crack in the bulk of a crystal. The results showed that pure tilt boundaries were several times tougher than single crystals: the method may be extended to technical alloys.

Microstructure Development in Thin Films During Deposition from the Vapor Phase. It is well recognized that the structure of a thin metallic film can be amorphous, polycrystalline or single crystal (epitaxial), depending upon the deposition process. In particular, the rate of deposition and the temperature of the substrate have important influences on the structure. It has been suggested that the grain structure of a polycrystalline film is determined by the nucleation density or by recrystallization effects, both of which are temperature-dependent.

In metal films made by thermal vapor deposition or by ion sputtering, we found that the grain size of the material, as deposited, depends linearly upon the film thickness when cold substrates are used. The results clearly indicate that grain growth occurs during the deposition process itself. The necessary thermal activation for recrystallization appears to derive

from the latent heat of solidification from the vapor phase. The occurrence of continuous recrystallization during film growth raises some interesting questions about the origins of grown-in film stresses.

Identification of the Failure Mechanism of a Compressively Loaded Thin Film on a Thick Substrate by Means of Synchrotron X-ray Topography Combined with Transmission Electron Microscopy. A compressively loaded thin film on a substrate is theoretically very stable, and its failure by delamination requires the existence of some form of stress concentration in order to nucleate a buckle. This failure mode is more common than would be expected on the basis of the theory. Using polycrystalline films on single crystal silicon wafers, we were able to measure the elastic deformation of the substrates with extreme accuracy using Synchrotron X-ray Topography (SXRT), and we also imaged the formation of localized deformation lines characteristic of film delamination when a certain film thickness is achieved. Electron microscopy of the same specimens reveals that the deformation is associated with bands of slip in the substrates, presumably generated by the stresses deriving from the overlayer film: the bands cause surface steps on the substrate, which provide the necessary stress concentration for delamination of the film by buckling.

Development of Grazing Bragg-Laue Synchrotron Topographic Techniques. White-beam synchrotron topographic techniques were developed in grazing Bragg-Laue geometries. These techniques examine the evolution of strain in the near-surface regions of single crystals undergoing phase transformations, in particular, for metal single crystals undergoing hydridation. Analysis of the projected lengths of dislocation images on topographs recorded by these techniques, incorporating the exploitation of the projective properties of the topographs, enabled the direct determination of X-ray penetration depths in single crystals diffracting in this geometry. The depth of penetration varied according to the distribution of localized strain fields in the crystal. In the regions immediately surrounding dislocation lines, penetration depths agreed with values predicted from kinematical theory. For regions of crystal where the local distortion field produces effective misorientations smaller than the rocking curve width of the perfect crystal, dynamical considerations are expected to be operative.

Synchrotron X-ray Topographic Studies of Electronic Materials. Synchrotron radiation was used to monitor the quality of single crystals of zinc cadmium telluride, quartz and gallium arsenide as a function of processing conditions. The technique was shown to be a powerful tool for such characterizations, giving unique insights as to how processing might be improved in these materials.

Synchrotron Topographic Studies of Nickel Base Alloy Jet Turbine Blades. Both reflection ACT and synchrotron white beam topographs of single crystal nickel base alloy jet engine turbine blades reveal that topography is far superior to previously used X-ray diffraction techniques for quality control of such blades. The use of white beam synchrotron X-ray topography should permit optimization of growth, annealing, and other processing of the materials of the blades in order to improve crystal perfection and hence improve mechanical and thermal properties.

Synchrotron X-ray Probing of Acoustic Waves. Transmission synchrotron X-ray topographs recorded from 0.5 inch diameter single crystals of aluminum which had been insonated with 20 kHz high power ultrasound revealed marked plastic deformation throughout the entire volume of the crystal that was caused by the ultrasound. This study provides direct evidence, for the first time, that high power ultrasound can move dislocations over large distances in metals.

Synchrotron X-ray Topographic Studies of Defects and Strain Fields in Metal-Semiconductor (Pd, Si) Interfaced Materials. A series of in situ absorption edge contour mapping experiments were carried out on metal-silicide specimens in the past year. A miniature fabrication chamber was constructed to enable in situ observations of the evolution of film stresses to be made during the deposition of the metal films, and during the subsequent annealing to allow the growth of silicides at the interfaces. Results obtained show that the residual film stress can be tailored by controlling the annealing process.

A Study of Creep Damage Using Synchrotron Microradiography. Synchrotron micro-radiographic techniques have been developed which can be used to quickly and reliably measure the amount of distribution of creep damage in a sample. This technique is made possible by the high brightness of the synchrotron source.

John Bilello
Past Subgroup
Representative

VUV RESEARCH OPERATIONS

Machine Operations

The UV ring was returned to operation from the Phase II shutdown essentially on schedule, with the first experiments being performed in late January. In addition to installing the Transverse Optical Klystron (TOK) and Infra-red beam lines, four of the eight dipole chambers were replaced, and new distributed ion pump elements, and clearing electrodes were installed. Also, a number of power supplies were replaced.

Unfortunately there were unplanned shutdowns during the remainder of 1987. A leak developed in the U2 front-end valve which necessitated venting the ring in May, in the time set aside for the installation of the TOK magnet. Problems were also experienced with the TOK water-cooled aperture, which required extra time to rectify. Subsequently, in late June, the aperture developed a leak from the cooling pipe to the ring and had to be removed. The following conditioning period was complicated by the fact that a considerable quantity of water had entered the ring. A new aperture was designed and installed in September, which was followed by the most successful conditioning of the UV ring to date. An integrated current of 43 Amp-hours was injected over four days including a peak current of 1.03 Amp.

Operations resumed with 5 bunch fills and injection over 700 mA. This conditioning performance was a great credit to the Vacuum and Operations Groups.

In September and October reliable high current operations were achieved with typical fills to 750 mA lasting about 5 hours with lifetimes of 150 minutes at 200 mA. Figure 1 shows graphically the total amp hours during FY 1987. Figure 2 shows the percentage breakdown of operations, studies, downtime (which includes injections/ramping time), maintenance, and conditioning.

Beam Line Operations

The past year saw a number of beam line developments on the UV floor. As mentioned, the TOK and IR beam lines were installed in the Phase II shutdown and are nearing operation. Radiation has been observed from both beam lines and characterization of the two sources has begun.

The prototype spherical grating monochromator, dubbed the "Dragon," was installed in record time on U4 and has given indications of spectacular resolution at full aperture, in excess of 1000 at the oxygen K-edge.

Other notable developments were the installation of a white light branch line on U3 and the addition of a transmission grating monochromator on U10A.

The second generation TGMs on U7 and U12 are nearing completion and work has begun on the ERG and TGM lines on U16. Also, the U8C zone plate monochromator is fully operational.

Finally, the University of Minnesota/ Argonne National Laboratory PRT vacated the U2 beamport in 1987.

VUV Studies and Upgrades

During the Phase II shutdown the following hardware was installed in the ring:

- the TOK wiggler,
- new quadrupole power supplies,
- new loop tuner for the main RF system, and
- a 200 MHz, 4th harmonic prototype RF system.

The TOK wiggler was successfully commissioned and the perturbation on the electron beam during normal operation, has been minimized.

The new loop tuners provide easier and more reliable control of the coupled bunch longitudinal instability.

The prototype 4th harmonic RF system, by lengthening the bunch and thereby reducing the Touschek scattering, improves the beam lifetime by 20-40%. A final system is now under design.

The construction of a resonant closed-orbit feedback system is being planned. This system should reduce by a factor of about 5 the low frequency orbit movements due to mechanical vibrations, and temperature variations. The magnitude of the present orbit movements is about 100 μm .

A low emittance configuration (5×10^{-8} m-rad at 750 MeV) was also successfully tested. The lifetime of the stored beam is severely limited by the Touschek effect.

Figure 1 Total Monthly Amp Hours on the NSLS VUV Ring During FY 1987.

Figure 2 Utilization of the VUV Ring for FY 1987 by Percentage in Time.

X-RAY RESEARCH OPERATIONS

Machine Operations

During the 1987 fiscal year there were five months of X-ray operations before the Phase II shutdown early in March 1987. During these five months, there were steady improvements in the amp hours of beam as displayed in Fig. 3 (which shows the total amp hours and the high energy amp hours). These improvements largely resulted from the installation of a third 52 MHz RF cavity in June 1986 which improved the ring vacuum by decreasing the required power levels in each of the cavities. Improvements also were made in the software ramp to avoid beam instabilities, thereby enabling higher current fills. The breakdown of the fiscal year into percentages of operations, studies, downtime (which includes injection/ramping time), maintenance and conditioning is shown in Fig. 4. The large percentage of time devoted to maintenance reflects seven months of Phase II shutdown work.

Beam Line Operations

The number of operating beam lines increased from 29 in FY 86 to 34 by March 1987, with the commissioning of the X10B, X10C (beam position monitor), X11B, X12B, X17T beam lines. The safety systems on beam line X21B and X23A3 were modified to allow different operating modes for new experiments.

Several changes were made to improve beam line operating conditions, which included changes in the procedures for the beam line vacuum so that the need for RGA scans is eliminated when front end pressure or beam line pressures fall below certain values. Several dedicated single-bunch shifts were scheduled for X18A and X24C and timing signals were provided. The unattended mode of X-ray operation was continued as was the parasitic use of studies shifts during periods when there are no injection/ramping studies.

In the area of user support an improved gas cylinder system was put into effect so that there would be a permanent stock of cylinders available on a sign-out basis. The BNL Ethernet system was made available to users. Also, by using a voice synthesizer the instantaneous X-ray and UV beam currents and messages displayed on channels 6 and 7 of the TV monitor were made available to users by dialing 282-5700. The poor quality of these messages will be upgraded in FY 88 in conjunction with other improvements in user communications. Towards the end of FY 87, the procedure for entering a user ILR (Intra-Laboratory Request) into the BNL system was greatly streamlined by directing work requests to the User Secretary. Also, a permanent, large (6000 liter), self-pressurizing, liquid nitrogen system was scheduled for installation in FY 88.

In July 1987 a major effort was made to render the X-ray floor and entire NSLS, clean and safe. The NSLS Housekeeping and Safety Committees will maintain these conditions in future. The additional storage and set-up space in the basement of Building 535 provided by the Phase II building expansion will facilitate this effort. An 80'x40' trailer also was assigned to the storage of user's packing boxes and 1.5 small trailers were assigned for the storage of user's equipment.

Before the shutdown, a number of modifications were made to the X-ray ring which provided crucial information. The first of these was the implementation of a prototype closed-orbit local feedback system on the X17T undulator beam line. Studies shifts were used to debug the system, and users observed negligible orbit shifts on their beam lines when the feedback was turned on and off. The feedback system stabilized the vertical and horizontal beam position to within $\pm 15 \mu\text{m}$ ($< 20 \mu$ radians of angle). A similar local feedback system will be employed on the Phase II insertion devices. In anticipation of the installation of the X5 LEGS chamber and magnets, the LEGS sextupole was installed in October 1986 to ensure that its effect on the X-ray orbit could be corrected.

In the fall of 1986, members of the Experimental Program Support Section met with each X-ray user group to determine what new beam lines, hutches, safety systems and utilities would be installed during the Phase II shutdown and what modifications would be required for existing beam lines. The extensive amount of work was needed. Ultimately an additional 27 beam lines would have to be installed, 9 of which would be on operating front ends (X9B, X10C, X15B, X20B, X23A2 and X26A), and 6 of which would result from moving the X13 and X21 beam lines to X7 and X3, respectively, to make room for new insertion device lines. When these new lines are completed, most of which are on bending magnets, the number of operating X-ray beam lines will almost double. With the assignment of an electrical engineer to the Experimental Program Support Section, it became possible to design an upgrade to the NSLS interlock system for installation on these new beam lines. The new design makes use of more compact, high reliability relays, of printed circuit boards to minimize wiring errors and facilitate maintenance, and of modularity to permit disconnection of the beam line safety system from the main interlock system for testing during normal operations. In FY87 the major prototype logic units were bench-tested and the prototype system will be installed on X7 in early FY88.

Figure 3 Total Monthly A.H./High Energy A.H. on the NSLS X-ray Ring During FY 1987.

Figure 4 Utilization of the X-ray Ring by Percentage in Time.

USER ADMINISTRATION

Introduction

Last year was a busy and productive one for the NSLS user community. This Section provides a brief overview of the events that occurred during the past year. The Informational Guides at the end of this Section outline the operational status, experimental capabilities available at each beam port/line, and contact personnel for those beam lines.

User Modes

The policy for experimental utilization of the NSLS is designed to enable the scientific community to cooperate in establishing comprehensive long-range experimental programs. Approximately 99 universities, 25 corporations, and 19 government institutions participate in research at the facility.

In addition to the beam lines constructed by the NSLS staff for general usage, a large number of beam lines were designed and instrumented by Participating Research Teams (PRTs). The PRTs are entitled to up to 75% of the operational time on their beam line(s) for a three-year term.

Insertion Device Teams (IDTs) were formed to design, fabricate, commission, and use wiggler and undulator beam lines. The conditions and terms are similar to those of the PRTs.

General users are scientists interested in using beam time at the NSLS facilities for experimental programs. They are scheduled by an independent allocation committee for a percentage of operating time for each beam line. Liaison and utilization support is provided to the General User by the cognizant beam line.

Proprietary research can be performed at the NSLS. The DOE granted the NSLS a Class Waiver, under whose terms the Proprietary User is obligated to pay the full cost recovery rate for using the NSLS. In return, the user has the option to take title to any inventions made during the research program and to treat as proprietary all technical data generated during that program.

Users Organization

The Users Organization met five times during FY 1987 to discuss various user-related issues such as housing, user support space, Phase II space allocation, Phase II shutdown scheduling, and the development of the General User scheduling and PRT tenure reviews.

Six subcommittees were appointed to address items of particular concern to the users. They were: 1) Phase II space allocation, 2) VUV ring scheduling, 3) X-ray ring scheduling, 4) orbit stability, 5) housing, office, and laboratory space, and 6) user accounting. Subcommittee reports are available upon request from the User Administration Office.

During the Annual Meeting, new members were elected to the Users Executive Committee (UEC) and to represent the Subgroups. These members are listed in Table 2.

Approximately 250 people attended the annual meeting on September 21-22. The program was dominated by scientific results germane to programs at the NSLS. Six keynote speakers and six plenary talks were presented during this meeting. Held in conjunction with the Users Meeting was the dedication ceremonies for the Phase II construction project. Following the dedication ceremony the PRTs displayed posters of work conducted at their beam line. In all, 145 posters were displayed.

In an effort to improve communications with the user community, a forum was held in the last session between more than 60 users and a panel of UEC, NSLS staff, and lab management. From the level of interest shown, this type of forum will be continued at future meetings.

General User Oversight Committee

The NSLS General User Oversight Committee (GUOC) was formed by the NSLS and the Users Executive Committee (UEC) to recommend allocations of beam time to the NSLS Chairman and to resolve conflicts that may arise between General Users, PRTs, IDTs, and NSLS staff. The Committee consists of five members; one NSLS scientist and two representatives from both the UV and X-ray community (see Table 3).

Thirty proposals were submitted for allocation of beam time by the GUOC for the May through August scheduling cycle on the UV ring. Twenty-four of these proposals were allocated beam time. Of the remaining six, three proposals were held pending completion of the beam lines requested, and for other reasons, three proposals were left for the subsequent scheduling cycle. Approximately ten General User proposals were allocated beam time on the X-ray ring before to the Phase II shutdown.

Although the present system is working well, during the past year it became apparent that scientific peer review will be necessary for certain disciplines. A The formation of a Proposal Study Panel is being discussed.

NSLS/HFBR Faculty Student Support Program

This program funded by the Department of Energy provides support for faculty/student research groups performing experiments at the NSLS as General Users, or neutron experiments at the BNL High Flux Beam Reactor (HFBR). The program is designed to encourage new users to these facilities and defray expenses incurred during exploratory visits to BNL, and during initial experiments at the NSLS and HFBR. It is aimed at university users having only limited grant support.

A three-member committee, consisting of one representative from the NSLS staff, one from the HFBR staff, and one designee of the NSLS Users Executive Committee, reviews applications and selects participants for the program.

Fifty-four faculty members and students participated in research on the X-ray and VUV rings at the NSLS and at the HFBR during FY 1987 with the help of this funding. Application forms or further information can be obtained from Susan White-DePace.

DOE High School Honors Research Program

For the second year in a row, Brookhaven hosted 56 high school students in the DOE High School Honors Research Program. The program was designed to encourage the development of scientific and technical talent in energy-related areas, emphasizing the type of research conducted at the NSLS. One outstanding student was chosen from each state, plus one each from the District of Columbia and Puerto Rico. In addition, students from Canada, Italy, Japan, and Mexico participated for the first time.

During the first three days of the program the students attended lectures on the nature of synchrotron radiation and its scientific applications, machine physics, operations, and procedures at the NSLS, and on the experiments which the students would be conducting. The weekend was devoted to calculations aimed at an understanding of the machine and its applications.

The second week was devoted to experiments at the NSLS facility. These experiments involved optical diffraction techniques for measuring laser light wavelengths, use of the photoelectric effect for determining the composition of a metal alloy (U7B and U14A), fluorescence spectrum of cyclohexane normalized by sodium salicylate fluorescence spectrum (U9A), photoionization yields of gaseous molecules (U11) and reflectivity of multilayer mirrors (U15). Tours also were provided by the Applied Science, Biology, Chemistry, HFBR, Medical, and Physics Departments.

The students used the final days of the program to prepare reports and present their experimental results and conclusions to the group as a whole. Copies of the program report are available from Don Metz, Office of Educational Programs.

All correspondence and inquiries regarding the NSLS facility should be addressed to:

Susan White-DePace, User Administrator
National Synchrotron Light Source Department
Building 725B
Brookhaven National Laboratory
Upton, NY 11973
(516) 282-7114

INFORMATIONAL GUIDE TO THE NSLS VUV BEAM LINES

Beam Port	Beam Line	Operational Status	Affiliation	Research Program	Monochromator	Local Contact	Spokesperson
U1	A	O	Exxon Research & Engineering	SEXAFS, ARUPS, XPS	ERG	Dale Sondericker (516)282-5501 (516)282-4983	Wolfgang Eberhardt (516)282-4983 (201)730-2567
	B	N	Exxon Research & Engineering	—	TGM	Mike Sansone (516)282-5759 (516)282-5501 (201)730-3388	Wolfgang Eberhardt (516)282-4983 (201)730-2567
U2	OPEN						
U3	A	O	LANL/Sandia/ U. of CA/LLL	Detector Calibration	ERG	Randy Alkire (516)282-5503	Walt Trela (505)667-1674
	B	N	LANL/Sandia/ U. of CA/LLL	Radiometry	—	Randy Alkire (516)282-5503	Walt Trela (505)667-1674
	C	O	LANL/Sandia/ U. of CA/LLL	Soft X-ray Spectroscopy	—	Randy Alkire (516)282-5503	Walt Trela (505)667-1674
U4	A	O	AT&T Bell Labs	ARUPS	TGM	Jack Rowe (201)582-5878 (516)282-5504	Jack Rowe (201)582-5878
	B	C	AT&T Bell Labs	UPS, SEXAFS, NEXAFS	SEM	Francesco Sette (516)282-5504 (201)582-3351 C.T. Chen (201)582-6030 (516)282-5504	Francesco Sette (201)582-3351 C.T. Chen (201)582-6030
U4IR		M	NSLS/AT&T Bell Labs/ Fairleigh Dickinson U./Exxon	Vibrational Spectroscopy of Molecules on Surfaces, Absorption, Fast Detectors	IR	Gryn Williams (516)282-3634	Gryn Williams (516)282-7529
U5		O	NSLS	Diagnostics	—	Ron Nawrocky (516)282-4449	John Galayda (516)282-4593
	U	O	BNL-Physics	Spin Polarized Angle Resolved UV Photoemission	TGM	Peter Johnson (516)282-3705	Peter Johnson (516)282-3705
U6		O	IBM	Lithography	White	Jerry Silverman (516)282-5506 (914)945-2099 John Warlaumont (914)945-1819	Alan Wilson (914)945-2759
U7	A	M	BNL-Physics/ NSLS/Exxon	XPS, SEXAFS	TGM	Francis Loeb (516)282-5507 (516)282-2092	Myron Strongin (516)282-3763
	B	O	BNL-Physics SUNY/@ Stonybrook	ARUPS, SEXAFS	PGM	Francis Loeb (516)282-5507 (516)282-2092	Myron Strongin (516)282-3763

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Beam Port	Beam Line	Operational Status	Affiliation	Research Program	Monochromator	Local Contact	Spokesperson
UB	A	O	IBM	ARUPS, NEXAFS	TGM	Amna Taleb-Ibrahimi (516)282-5508 (516)282-5303	Read McFeely (914)945-2068
	B	O	IBM	ARUPS, NEXAFS	TGM	Amna Taleb-Ibrahimi (516)282-5508 (516)282-5303	Read McFeely (914)945-2068
	C	O	IBM	Evaluation of a Zone Plate Monochromator, Reflectivity Measurements of Thin Films and Multilayers	Zone Plate	Eberhard Spiller (914)945-2447	Eberhard Spiller (914)945-2447
	D	O	IBM	Scanning Soft X-ray Microscopy	Microscope	Eberhard Spiller (914)945-2447	Eberhard Spiller (914)945-2447
U9	A	O	NSLS/BNL-Chemistry	Fluorescence Lifetimes Photoconductivity, Photoionization	S-N	Jack Preses (516)282-5509 (516)282-4371	Ralph Weston (516)282-4373
	B	O	NSLS/BNL-Biology	CD, MCD, Fluorescence Lifetimes	C-T	John Sutherland (516)282-5509 (516)282-3406	John Sutherland (516)282-3406
U10	A	O	U. of TN/ORNL/NBS	X-ray Fluorescence, Soft X-ray Emission, Soft X-ray Absorption, Electron Spectroscopy	SXES	King Tsang (516)282-5510	Tom Callcott (615)974-7848
	B	O	NSLS/Superconducting Super Collider	Stimulated Desorption	White	Joe Schuchman (516)282-4630	Joe Schuchman (516)282-4630
U11		O	NSLS/BNL-Chemistry U. of NM/ANL/Yale U./ORNL/Boston U.	Gas Phase Photoionization	NIM	Mike White (516)282-5511 (516)282-4345	J. Robb Grover (516)282-5511 (516)282-4348
U12	A	C	U. of PA/ORNL	High Resolution Core Level Spectroscopy	TGM	Xiaohu Pan (516)282-5512 (516)282-5210	Ward Plummer (215)898-8157 David Zehner (615)574-6291
	B	O	U. of PA/ORNL	ARUPS	TGM	Xiaohu Pan (516)282-5512 (516)282-5210	Ward Plummer (215)898-8157 David Zehner (615)574-6291
	C	C	U. of PA/ORNL	Infrared Vibration Spectroscopy	C-T	David Heskett (215)898-7987	Ward Plummer (215)898-8157
U13	TOK	M	NSLS/AT&T Bell Labs	TOK Wiggler		Anne Marie Fauchet (516)282-5028	Anne Marie Fauchet (516)282-5028
	U	C	NSLS/Drexel U./U. of Wisconsin @ Milwaukee/Montana St. U./Brandeis U./AT&T Bell Labs	High Resolution VUV/Soft X-ray Electron and Ion Spectroscopies	SGM	Steve Hilbert (516)282-7570	Wayne Ford (406)994-6156 Steve Hilbert (516)282-7570

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Beam Port	Beam Line	Operational Status	Affiliation	Research Program	Monochromator	Local Contact	Spokesperson
U14	A	O	NSLS	Solid State Photoemissions Studies	PGM	Carol Hirschmugel (516)282-5514 (516)282-7253	Richard Garrett (516)282-4245
U15		O	NSLS/SUNY @ Stonybrook/ IBM/LEL	Soft X-ray Spectroscopy, Contact Microscopy	TGM	Waiman Ng (516)282-5515	Janos Kirz (516)632-8106 (516)282-4723
U16	A	C	Cornell U./ U. of TX/Sandia	ARUPS, SEXAFS, XPS, NEXAFS, ERG Stimulated Desorption		Thor Rhodin (607)255-4068	Thor Rhodin (607)255-4068
	B	P	Cornell U./ U. of TX/Sandia	Molecular Beam Scattering Solid State Photoemission Soft X-ray Spectroscopy	S-N	Robert Merrill (607)255-7504	Robert Merrill (607)255-7504
	C	C	U. of TX/Sandia	Angle-resolved Photo- electron Emission, Spin- Polarized Photoelectron Emission, Epitaxial Metal Films	TGM	James Erskine (512)471-1464	James Erskine (512)471-1464

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INFORMATIONAL GUIDE TO THE NSLS X-RAY BEAM LINES

Beam Port	Beam Line	Operational Status	Affiliation	Research Program	Local Contact	Spokesperson
X1	A	C	NSLS/SUNY @ Stony Brook/ IBM/LLNL	Soft X-ray Imaging	Harvey Rarback (516)282-3758 (516)282-5601	Harvey Rarback (516)282-3758
	B	M	Exxon Research & Engineering	Spectroscopy	Wolfgang Eberhardt (201)730-2567 (516)282-4983 (516)282-5701	Wolfgang Eberhardt (516)282-4983 (201)730-2567 (516)282-5701
X2	A	P	ANL/NSLS/Brooklyn College @ CUNY/NC State U./ Northwestern U./Standard Oil/U. of MI	Scattering, Small Angle Scattering, Diffraction	Mati Bloch (516)282-3641	Gopal Shenoy (312)972-5537
	B	P	ANL/NSLS/Brooklyn College @ CUNY/NC State U./ Northwestern U./Standard Oil/U. of MI	Time & Space Resolved Dispersive X-ray Spectroscopy	Tim Morrison (312)972-5539	Gopal Shenoy (312)972-5537
X3	A1	P	State U. of NY	Short Wavelength Crystallography, Diffraction, and Scattering	Jim Phillips (516)282-5603 (516)282-3770	Phil Coppens (716)831-3911
	A2	O	State U. of NY	Diffraction, X-ray Spectroscopy, Crystallo- graphy, Scattering, Small-angle Scattering	Jim Phillips (516)282-5603 (516)282-3770	Phil Coppens (716)831-3911
	B	O	State U. of NY	X-ray Spectroscopy, Surface Physics	Jim Phillips (516)282-5603 (516)282-3770	Phil Coppens (716)831-3911
X4	A	N	Howard Hughes Medical Institute (Columbia U.)	Multiwavelength anoma- lous Diffraction Analysis of Crystalline Biologi- cal Macromolecules	Jean-Louis Staudermann (212)305-1846 (516)282-3132	Wayne Hendrikson (212)305-3456
	C	N	Howard Hughes Medical Institute (Columbia U.)	Diffraction Measurements from Biological Macro- molecules	Jean-Louis Staudermann (212)305-1846 (516)282-3132	Wayne Hendrikson (212)305-3456
X5	A	N	BNL-Physics	LEGS, Medium Energy Nuclear Physics	Andy Sandoz (516)282-7951	Andy Sandoz (516)282-7951
X6	A	N	Exxon Research & Eng.	X-ray Tomography	Kevin D'Amico (516)282-2065 (201)730-2891	Kevin D'Amico (516)282-2065 (201)730-2891
X7	A	O	NSLS/BNL-Physics/U. of PA/ State U. of NY/Allied/Signal/ Dupont/Carnegie Inst. of WA/ Union Carbide/Alfred U./ Mobil/U. of CA @ Santa Barbara	Powder Diffraction	Dave Cox (516)282-5607 (516)282-3818	Dave Cox (516)282-3818 (516)282-5607

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Beam Port	Beam Line	Operational Status	Affiliation	Research Program	Local Contact	Spokesperson
X7	B	O	NSLS/BNL-Chemistry/ U. of Pittsburgh/ Swedish Research Council/ Mobil Research & Development Corp.	Crystallography, Wide Angle Scattering	Ake Kvick (516)282-5707 (516)282-4381	Ake Kvick (516)282-5707 (516)282-4381
X8	A	M	LANL/Sandia/LNL/ U. of CA	Photoelectron and Photoion Spectroscopy	Randy Alkire (516)282-5503 (516)282-5520	Roger Bartlett (505)667-5923
	C	M	LANL/Sandia/LNL/ U. of CA	EXAFS, Diffraction	Randy Alkire (516)282-5503 (516)282-5520	Walt Trela (505)667-1674
X9	A	O	National Bistructures Research Resource	EXAFS	Syed Khalid (516)282-5609	Grant Barker (215)386-1912
	B	P	National Bistructures Research Resource	Scattering, Diffraction	Syed Khalid (516)282-5609	Kent Blasie (215)898-6208
X10	A	O	Exxon Research & Engineering	Scattering, Small Angle Scattering, Diffraction, Crystallography	Kevin D'Amico (516)282-2065 (516)282-5610 (201)730-2891	Dave Moncton (516)282-2741 (201)730-2384
	B	O	Exxon Research & Engineering	Crystallography, Scattering	Kevin D'Amico (516)282-5610 (516)282-2065 (201)730-2891	Dave Moncton (516)282-2741 (201)730-2384
	C	C	Exxon Research & Engineering	EXAFS	Kevin D'Amico (516)282-2065 (516)282-5610 (201)730-2891	Dave Moncton (516)282-2741 (201)730-2384
X11	A	O	NC State U./U. of CT/BNL/ U. of WA/Mobil/Dupont/ ANL/Celanese/U. of Notre Dame/GA Tech U./LLL	EXAFS	Steve Heald (516)282-5611 (516)282-2861	Dale Sayers (919)737-3482
	B	C	NC State U./U. of CT/BNL/ U. of WA/Mobil/Dupont/ ANL/Celanese/U. of Notre Dame/GA Tech U./LLL	EXAFS	Steve Heald (516)282-5611 (516)282-2861	Dale Sayers (919)737-3482
X12	A	O	NSLS	Diagnostics	Peter Siddons (516)282-2738	Peter Siddons (516)282-2738
	B	M	NSLS/BNL-Biology	Small Angle Scattering	Malcolm Capel (516)282-5712 (516)282-2792	Malcolm Capel (516)282-2792
	C	O	BNL-Biology	Protein Crystallography	Bob Sweet (516)282-5712 (516)282-3401 (516)282-5642	Bob Sweet (516)282-3401 (516)282-5642
X13			NSLS	R&D Optics Development Soft X-ray Utilization	Erik Johnson (516)282-4603	Erik Johnson (516)282-4603

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Beam Port	Beam Line	Operational Status	Affiliation	Research Program	Local Contact	Spokesperson
X14	A	O	ORNL/Oak Ridge Associated Universities Users Association	Scattering, Crystallography, Spectroscopy	Gene Ice (516)282-5614	Gillie Sparks (615)574-6996
X15	A	O	AT&T Bell Labs	X-ray Standing Wave, Soft X-ray Spectroscopy, X-ray Lithography	Brian Kincaid (516)282-5615	Brian Kincaid (516)282-5615
	B	M	AT&T Bell Labs	SEXAFS, EXAFS	Alastair MacDowell (516)282-3565	Paul Citrin (201)582-5275
X16	A	O	AT&T Bell Labs	Surface Diffraction	Alastair MacDowell (516)282-3565 (516)282-5716	Paul Fuoss (201)949-3581 Ian Robinson (201)582-6056
	B	O	AT&T Bell Labs	Diffraction	Alastair MacDowell (516)282-3565 (516)282-5716	Denis McWhan (516)282-5716 (516)282-3927 (201)582-4557
	C	O	AT&T Bell Labs	Diffraction	Alastair MacDowell (516)282-3565 (516)282-5716	Denis McWhan (516)282-5716 (516)282-3927 (201)582-4557
X17	B1	C	NSLS	Materials Sciences Chemical Crystallography, EXAFS, High Pressure Physics, Topography, X-ray Scattering	Dean Chapman (516)282-5617 (516)282-4744	Bill Thomlinson (516)282-3937
	B2	C	NSLS/SSRL/Stanford U. / LBL/ BNL-Medical	Angiography, Radiotherapy	Bill Thomlinson (516)282-5617 (516)282-3937	Bill Thomlinson (516)282-3937
	C	C	NRL/LLNL/U. of WA/ U. of CA @ Berkeley/ Exxon/U. of HI/ Carnegie Inst. of WA/ AT&T Bell Labs/SUNY @ Stony Brook/Cornell U./LANL	High Pressure	Denis McWhan (516)282-3927	Earl Skelton (202)767-3014
X18	A	O	Matrix	Diffuse & Surface Scattering	Steve Ehrlich (516)282-5618 (516)282-7862	Gerry Liedl (317)494-4095
	B	O	West Virginia U. / U. of Pittsburgh/Chevron/ Allied-Signal Research/ GTE/Brooklyn College of CUNY	EXAFS	Mohan Ramanathan (516)282-5718 (516)282-7860	Pedro Montano (304)293-3422 (718)780-5779
X19	A	M	NSLS	X-ray Spectroscopy, EXAFS	Peter Stefan (516)282-5619 (516)282-2117	Peter Stefan (516)282-2117

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Beam Port	Beam Line	Operational Status	Affiliation	Research Program	Local Contact	Spokesperson
X19	C	O	NSLS/Synchrotron Topography Project Consortium	Topography	Tony Hmelo (516)282-5719 (516)632-8500	Michael Dudley (516)632-8500
X20	A	O	IBM/MIT	Scattering, EXAFS	Jean Jordan-Sweet (516)282-5720	Paul Horn (914)945-2445
	B	C	IBM/MIT	Scattering at Fixed Energy	Jean Jordan-Sweet (516)282-5720	Paul Horn (914)945-2445
	C	O	IBM/MIT	Scattering, EXAFS	Jean Jordan-Sweet (516)282-5720	Paul Horn (914)945-2445
X21		N	NSLS	High Energy Resolution Inelastic Scattering	Jerry Hastings (516)282-3930	Jerry Hastings (516)282-3930
X22	B	O	BNL-Physics/ Harvard U.	High Resolution X-ray Diffraction	Ben Ocko (516)282-5622 (516)282-4299	John Axe (516)282-3821
	C	O	BNL-Physics	Diffraction Studies of Magnetic and Structural Phase Transformations, Surface Scattering	Doon Gibbs (516)282-5622 (516)282-4608	John Axe (516)282-3821
X23	A2	M	National Bureau of Standards	EXAFS, SEXAFS, with Standing Wave & Photoelectron Detection, Specular X-ray Reflection	Richard Spal (516)282-5623 (516)282-2279	Masao Kuriyama (301)975-5974
	A3	O	National Bureau of Standards	Real Time Topography, Microradiography, Energy Dispersive Diffraction, White Beam Experiments, EXAFS	Richard Spal (516)282-5623 (516)282-2279	Masao Kuriyama (301)975-5974
	B	O	Naval Research Lab	Scattering, Crystallography, EXAFS	John Kirkland (516)632-8515 Richard Neiser (516)282-5723 (516)282-2258	W. T. Elam (202)767-3014
X24	A	O	National Bureau of Standards	X-ray Spectroscopy, Atomic & Molecular Physics	Barry Karlin (516)282-5624 Paul Cowan (301)975-4846	Richard Deslattes (301)975-4841
	C	O	Naval Research Lab	Photoemission and Reflectance Spectroscopy	Jack Rife (516)282-5624 (202)767-4654	Milton Kabler (202)767-2223
X25		C	NSLS/AT&T Bell Labs/IBM/ Harvard U./BNL-Physics/ Exxon	High-Q Resolution Elastic Scattering	Lorrey Berman (516)282-5625	Lorrey Berman (516)282-5625

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Beam Port	Beam Line	Operational Status	Affiliation	Research Program	Local Contact	Spokesperson
X26	A	P	BNL-DAS/U. of Chicago/DOE/ NIH Biotechnology Research/ Cornell U./Texas A&M/ U. of TN	Microprobe	Keith Jones (516)282-5626 (516)282-4588 (516)282-5726	Keith Jones (516)282-4588
	C	O	BNL-DAS/U. of Chicago/DOE/ NIH Biotechnology Research/ Cornell U./Texas A&M/ U. of TN	Atomic Physics	Keith Jones (516)282-5626 (516)282-4588 (516)282-5726	Keith Jones (516)282-4588
X27		C	NSLS	Instrument & Diagnostic Development	Peter Siddons (516)282-2738	Peter Siddons (516)282-2738
X28		C	NSLS	Instrument & Diagnostic Development	Peter Siddons (516)282-2738	Peter Siddons (516)282-2738

O = Operational (beam line is actively used in research); M = Commissioning (beam line is built but is being run for the sole purpose of detecting flaws in the configuration); C = Construction (beam line is being assembled); P = Planned (beam line design is completed but construction has not yet begun); N = Conceptual (pre-design stage). ARUPS = angle-resolved ultraviolet photoemission spectroscopy; XPS = X-ray photoemission spectroscopy; EXAFS = extended X-ray absorption fine structure; SEXAFS = surface EXAFS; ERG = extended range grasshopper; CD = Circular dichroism; C-T = Carney-Turner; IR = Infrared Interferometer, LEGS = Laser Electron Gamma Source; MCD = Magnetic CD; PGM = plane grating monochromator; TGM = toroidal grating monochromator; NIM = normal incidence monochromator; SGM = Spherical Grating Monochromator, S-N = Seya-Namioka, and SXES = soft x-ray emission spectrometer, TOK = Transverse Optical Krypton; UPS = ultraviolet photoemission spectroscopy; NEXAFS = near edge x-ray absorption fine structure.

NOTES: Local Contact: individual(s) usually available at the beam line, their telephone number and the location of that number.

Spokesperson: individual(s) responsible for the beam line research program, their telephone number and the location of that number.

Research Program: describes only broad or general categories of research; specifics should be discussed with the beam line personnel.

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SECTION 2

REPORTS OF THE VUV RESEARCH AT THE NSLS

This section contains the reports of research carried out at the NSLS VUV storage ring during the 1987 fiscal year. Most of the contributions have been specifically written for this annual report by the experimenters. Their efforts are greatly appreciated by the annual report staff. The reports are presented by beam line and are arranged alphabetically by first author (except where a specific order was requested.) The Table of Contents that follows is also arranged by beam line and first author.

VUV Storage Ring Parameters as of June 1987	
Parameters	VUV Storage Ring
Normal Operating Energy	0.750 GeV
Design Current (multibunch operation)	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	~3.00 meters
$\lambda_c(E_c)$	25.3 Å (486 eV)
$B(\rho)$	1.28 Tesla (1.91 meters)
Electron Orbital Period	170.2 nanoseconds
Damping Times	$\tau_x \simeq \tau_y \simeq 17$ msec; $\tau_z \simeq 9$ msec
Touschek lifetime dependent on current/bunch and vertical emittance	
Lattice Structure (Chasman-Green)	Separated Function, Quad, Doublets
Number of Superperiods	4
Magnet Complement	8 Bending (1.5 meters each) 24 Quadrupole (0.3 meters each) 12 Sextupole (0.2 meters each)
Nominal Tunes ν_x, ν_y	3.12, 1.17
Momentum Compaction	0.023
R.F. Frequency	52.887 MHz
Radiated Power	14.7 kW/amp of Beam
R.F. Peak Voltage	100 kV
Design R.F. Power	50 kW
ν_s (Synchrotron Tune)	0.002
Natural Energy Spread (σ_e/E)	4.5×10^{-4}
Natural Bunch Length (2σ)	7.6 cm ($I < 20$ mA)
Horizontal Damped Emittance (ϵ_x)	1.5×10^{-7} meter-radian
Vertical Damped Emittance (ϵ_y)	$\geq 2.8 \times 10^{-10}$ meter-radian (adjust.)
Power per Horizontal milliradian, 1A	2.3 Watts
Source Size: σ_h, σ_v	0.5 mm, > 0.06 mm

Source of Data: NSLS Parameters, January 1983, compiled by A. van Steenberg; updated values provided by Gaetano Vignola (NSLS).

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The absorption of a soft x-ray photon by an isolated molecule leads to a chain of events the ultimate result of which is the fragmentation of the molecule. Initially a highly excited core hole state is created. This state decays via a radiationless two electron transition. The final state of this transition has multiple holes in the valence shell and these are the unstable configurations that lead to the production of ionic and neutral fragments. In order to identify the pathways of the soft x-ray induced fragmentation one has to characterize the final electronic configurations of the molecule after the core hole decay by measuring the kinetic energy of the ejected Auger electron. The ions are then recorded in coincidence with the various final states of the core hole decay.

Using the quasimonochromatic undulator beam at the X17T spectroscopy beamline we have studied these processes for various molecules including N_2 , N_2O , and CO_2 . Here we want to just give an example by showing the ion spectra of N_2O in Fig. 1, taken in coincidence with the Auger decay of an O-core hole. The mass to charge ratio of the ions is measured by the time of flight of the product and the most likely assignment is indicated above each peak.

The ion spectra in the top panel of Fig. 1 are taken in coincidence with the leading Auger peak of the O-Auger decay of N_2 , which is assigned to a $[2\pi^{-2}]$ double hole configuration. The ion spectra show that this electronic final state of the core hole decay results in the production of N^+ and NO^+ as the major decay channel. This is not unexpected because the 2π orbital is bonding between the two Nitrogen atoms in the linear NNO molecule.

In the next panel (B) of Fig. 1 we see not only N^+ and NO^+ but also the complementary channel of O^+ and N_2^+ . The hole configurations we are taking these ions in coincidence with are $[1\pi^{-1}, 2\pi^{-1}]$ and $[6\sigma^{-1}, 2\pi^{-1}]$.

In panels C and D we do not observe any N_2^+ and NO^+ anymore. Now the molecule falls apart completely and in some of the events a neutral third fragment has to be produced. The hole configurations are $[6\sigma^{-1}, 1\pi^{-1}]$ for panel C and $[5\sigma^{-1}, 6\sigma^{-1}]$ as well as $[4\sigma^{-1}, 5\sigma^{-1}]$ for panel D. The 4σ and 5σ orbitals are bonding throughout the molecule and therefore it is not surprising to find the molecule completely fragmented upon removal of these electrons.

Auger-electron ion coincidence studies like the ones presented here reveal the involvement of individual valence electrons into the formation of the molecular bond. Measuring also the kinetic energy distribution of the ionic fragments observed, in some cases we can even directly determine the potential energy surfaces of the highly excited states populated in the decay of the initial core hole excitation.

These experiments were carried out on X17T at the NSLS. This program was partially supported by NSF under contract No. NSF-DMR-851919.

N_2O Auger Electron Ion Coincidences

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Our Fluorescence Yield Near Edge Spectroscopy (FYNES) program has been focussed on a detailed study of the interaction of coadsorbed CO and hydrogen on the Ni(100) surface for hydrogen pressures up to 10 torr. During these studies, we discovered that chemisorbed CO is displaced by more weakly adsorbed hydrogen for hydrogen pressures above 10^{-4} Torr in a matter of minutes in the 290 to 330 K temperature range. The discovery of this unexpected surface reaction highlights the importance of surface methods which allow adsorbed monolayers to be characterized in the presence of reactive environments. Detailed spectroscopic examination of coadsorbed CO and hydrogen using FYNES indicates that no detectable changes of either the orientation or bonding of chemisorbed CO are caused by coadsorbed hydrogen over a wide range of temperatures and hydrogen pressures. These high pressure experiments were performed with dilute mixtures of CO in hydrogen (1-100 ppm) so that large CO coverages could be maintained in the presence of hydrogen pressures above 10^{-4} torr.

Several series of experiments were performed to characterize the kinetics and mechanism of hydrogen displacement of chemisorbed CO. As indicated in Fig. 1, the Fluorescence Yield intensity of the π resonance of adsorbed CO was used to monitor the displacement of CO in real time in the presence of gaseous H_2 . A series of in-situ transient Fluorescence Yield Near Edge Spectroscopy experiments have been performed over the 10^{-4} to 1 torr pressure range to characterize the kinetics of the displacement reaction illustrated in Fig. 2. The reaction is first order in CO coverage with an abrupt decrease in rate with decreasing CO coverage. The activation energy of the displacement reaction is 8 kcal/mole in the high coverage region and 12 kcal/mole for low coverages. The reaction kinetics are 0.4 order in hydrogen pressure over the 10^{-5} to 10^{-2} torr range.

A series of thermal desorption experiments were performed to confirm that displacement occurs and to check the validity of the FYNES kinetic results. Rapid displacement of adsorbed CO by hydrogen was observed. The kinetic results obtained using the thermal desorption method agree with the more complete kinetic results obtained with FYNES. In addition, the thermal desorption results suggest that the abrupt decrease in displacement rate is correlated with the increase in heat of adsorption observed with decreasing CO coverages. A series of displacement experiments were performed in order to characterize the mechanism of the displacement reaction. No displacement is observed with He, Ne, Ar, CH_4 , and N_2 for pressure up to 10^{-3} torr. D_2 gives displacement rates within 5% of those observed for H_2 . Taken together these results suggest that direct energy transfer between "hot" recently formed hydrogen atoms and chemisorbed CO is furnishing part of the energy required for displacement. Thermal energy from the surface is furnishing the remainder of the energy required to desorb CO from the surface.

Fig. 1 Displacement of a monolayer of chemisorbed CO by 9×10^{-4} torr of hydrogen occurs in less than 600 sec at 300 K. The inset spectra illustrate normalized CO spectra with normal and glancing incidence light for a CO saturated surface at 100K.

Fig. 2 The logarithm of CO coverage taken from transient FYNES experiments, as a function of displacement time for several temperatures. Reaction rates in the 10^{-2} monolayer/sec to 10^{-5} monolayer/sec can be characterized using this in-situ technique.

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We have used total electron yield to study the near edge x-ray absorption fine structure (NEXAFS) of the La 4d edge in La_2CuO_4 (Fig. 1). The spectrum is typical for La-based compounds and is characterized by two sharp peaks below the 4d threshold and giant resonance peak with a maximum at about 25 eV above threshold. The decay of these 4d core electron excitations causes resonant enhancement of the La photoemission features, which will be used to identify the La contribution to the valence band photoemission. To observe which channels are activated in the deexcitation of the La core to bound transition, photoemission spectra with incident photon energies indicated by the arrows in Fig. 1 were collected and normalized to the incident photon flux. As can easily be seen, the photoemission spectrum "e" taken with $h\nu=118$ eV, the maximum in the giant absorption peak, shows enhancement of the La 5s, $5p_{1/2}$, and $5p_{3/2}$ emission and in the La-Auger $\text{N}_{4,5}\text{O}_{2,3}\text{V}$ channels. Not so obvious, but nevertheless more interesting to the problem of high- T_c superconductors, is what is occurring in the valence band. The cross sections for Cu and O are lower for an incident photon energy of $h\nu = 118$ eV than for 113.5 eV. Therefore the enhancement in the difference spectra "e-d" of Fig. 2 at 3.5 eV below E_F is a La-derived feature.

The peaks at 9.5 and 11.5 eV do not exhibit any comparable resonant enhancement. Relative to the Cu and O emission the La derived states are located near the top of the strongest valence band peak whereas Mattheis³ calculates the La features to contribute mostly to the high energy side of the peak. However the density of states calculations do not represent the valence band photoemission in general, due to hole localization. Therefore any comparison with these calculations has to be viewed with caution. If, for example, the La states are more delocalized than the O and Cu states, then the relative shift between the calculated and experimental valence bands could be explained. The resonant photoemission from the spike at $h\nu=101.5$ eV depicted in curve "b" of Fig. 2 shows enhancement of the La 5s and $5p_{1/2}$ emission but not of the $5p_{3/2}$. This work was performed at the EXXON U-1 beamline at the NSLS which is supported by the DOE.

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¹ L. F. Mattheis, Phys. Rev. Lett. **58**, 1028 (1987).

Fig. 1 La 4d absorption edge in La_2CuO_4 .

Fig. 2 Normalized photoemission spectra of La_2CuO_4 taken at the photon energies indicated by the arrows in Fig. 1. The arrows mark the Auger $\text{N}_{4,5}\text{O}_{2,3}\text{V}$ emission.

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Valence band photoemission spectra of superconducting, Sr-doped $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ and of the base oxide La_2CuO_4 have been studied on the EXXON beamline U1. The samples were introduced into the UHV chamber by means of a transfer line. Cleaning was done by Ar and O ion sputtering or by scraping with a tungsten carbide file. All data were collected at room temperature and no changes in the data were observed as a function of time.

Photoemission measurements of the valence bands of La_2CuO_4 and $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ taken at photon energies of $h\nu = 100$ eV and 50 eV are shown in Fig. 1. The curves are comprised of three peaks. The large peak with its maximum at 4.8 eV is mainly composed of an overlap of the Cu $3d(x^2-y^2)$ and O $2p$ bands. The peak at 9.5 eV is probably due to C contamination and the peak at 11.5 eV is a shake up satellite. As can be seen, there is very little difference between the superconductor and the base oxide. The inset of Fig. 1 shows the Fermi level of La_2CuO_4 multiplied times 50 compared to a Pt foil. From this we conclude that there is a very low but measurable density of states at the Fermi level. The Fermi level shifted by <100 meV upon doping in the superconducting sample relative to the base oxide.

Fig. 1 Photoemission spectra of (a) $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ and (b) La_2CuO_4 at $h\nu=100$ eV and $h\nu=50$ eV. The dashed line is from a Pt standard. The inset shows the Fermi level of $\text{La}_2\text{CuO}_4 \times 50$ compared to Pt.

Fig. 2 Experimental valence band (dashed line) compared to Mattheiss density of states calculation (solid line) of La_2CuO_4 . The calculated curve has been shifted down to higher binding energy by 1.5 eV.

Fig. 2 shows the experimental valence band compared to the density of states calculation of Mattheiss.¹ Lining up the center of gravity of the largest valence band peak, we find a shift of 1.5 eV between the experimental and theoretical curves. This discrepancy could be due to a localization of the final state hole, which is not correctly described in the delocalized band picture. The presence of the shake up peak in the valence band as well as the core level photoemission satellites indicates the importance of hole localization and screening in these materials. These experiments were performed at beamline U1 at the NSLS, which is supported by the DOE.

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¹L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

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Interface Structure can be studied on an atomic scale by growing the interface, monolayer by monolayer, and observing the evolution of the electronic structure as a function of layer thickness. Here we report such a study using photoemission spectroscopy on hydrogenated amorphous silicon (a-Si:H) and silicon nitride (a-SiN_x:H, $X \approx 1.33$) heterojunctions made by plasma assisted CVD. The experimental techniques for heterojunction fabrication, in-situ sample transfer and photoemission measurements are the same as in our previously reported work on amorphous silicon and silicon oxide interfaces.¹

Figure 1(a)-(d) shows the Si-2p core level spectra measured at photon energy $h\nu = 120$ eV for a-Si:H overlayers deposited on a-SiN_x:H. The photoemission intensity of the Si overlayer is given by the peak centered at binding energy of 99.6 eV. It was obtained by subtracting from the measured photoemission intensity (full curve) the contribution due to the SiN_x underlayer given by the peak centered at 101.2 eV. We find that the Si overlayer peak coincides with the peak corresponding to Si coordinated with four Si atoms even for the first few monolayers. This indicates that the Si atoms in the overlayer are bonded predominantly to the Si atoms in the a-SiN_x:H substrate forming an atomically abrupt interface. Similar bonding of the Si atoms was also observed in the case of a-Si:H overlayers on a-SiO_x:H.¹ Unlike SiO_x on Si interface where significant plasma oxidation was observed causing a graded region over ≈ 5 Å, SiN_x on Si interface was found also atomically abrupt indicating that nitridation is rather weak.

Valence band photoemission on heterojunctions was measured and gave a value of 1.2 ± 0.2 eV for the band offset between a-Si:H and a-SiN_x:H which is in agreement with previous measurements.² Other important information obtained from the valence band EDC's and Si L_{2,3} absorption edge measured by yield spectroscopy as a function of overlayer thickness for both a-Si:H and a-SiN_x:H are discussed in detail elsewhere.³

The photoemission experiments were performed at beamline U1 at the NSLS, which is supported by the DOE.

Fig. 1 Si-2p core level spectra for a-Si:H overlayers grown on a-SiN_x:H. Overlayer thicknesses are indicated.

VIBRATIONALLY RESOLVED ELECTRONIC AUTOIONIZATION OF CORE-HOLE RESONANCES

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Vibrational motions of molecular ions are influenced by resonant excitation, and conversely, fundamental aspects of resonant molecular ionization are illuminated by probing the vibrational motion of molecular ions. However, vibrationally resolved studies following resonant excitation of core electrons have been beyond the reach of traditional photoionization studies. Using N_2 as an example, we demonstrate that dispersed fluorescence measurements from electronically excited valence hole state ions circumvent limitations imposed by alternative methods, and in so doing, provide completely vibrationally resolved data. Recent theoretical studies and experiments have investigated the decay of molecular core-hole resonances into the (single) valence hole states of the molecular ions. A novel aspect of autoionization for core hole resonances is that lifetime broadening results in overlapping vibrational levels of the core-excited state. The studies presented here demonstrate that dispersed fluorescence measurements provide an excellent means of investigating such effects.

The excitation-fluorescence sequence used for the present studies is represented schematically by the following equation.

where v' and v'' are the vibrational levels for the ion in the excited ($B^2\Sigma_u^+$) and ground ($X^2\Sigma_g^+$) valence-hole states, respectively, and $h\nu_{v'-v''}$ is the energy separation between these levels.⁸

Figure 1 shows two fluorescence spectra. The spectrum obtained at $h\nu = 50$ eV is a nonresonant spectrum, and $h\nu = 401$ eV corresponds to the peak of the $1s+1\pi^*$ resonance. These spectra cover the region of the $v' = 0 \rightarrow v'' = 1$ and $v' = 1 \rightarrow v'' = 2$ ($B \rightarrow X$) fluorescence transitions, and they demonstrate that the cross section for the $v' = 1$ level increases relative to that of $v' = 0$ for resonant excitation. These results are currently being analyzed to assess the importance of lifetime induced vibrational interference, and the key point is that these results give completely vibrationally resolved data, thereby permitting quantitative comparison with theory.

Figure 1. Fluorescence spectrum of $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ showing $v' = 0 \rightarrow v'' = 1$ and $v' = 1 \rightarrow v'' = 2$ transitions following nonresonant excitation ($h\nu = 50$ eV), and resonant excitation ($h\nu = 401$ eV, $1s+1\pi^*$).

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* Research sponsored by the National Science Foundation and the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under grant number AFOSR-84-0261.

† Supported by the US Department of Energy through its division of Chemical Sciences, Office of Basic Energy Sciences.

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To date, there exists no general procedure to predict when a surface resonance might occur and what its properties might be. This is unfortunate since resonant states enable "communication" between surface and bulk layers, and thus might be important in determining such phenomena as surface reconstructions and electric dipole layer formation. The difficulty in predicting the occurrence of a surface resonance arises from the uncertainty of how strongly it will couple to the bulk states with which it is degenerate. If the coupling is too strong, the resonance will be broadened to such an extent that it becomes too diffuse to observe. In the case of coupling to the bulk through the spin-orbit interaction, the coupling will usually be weak and characterization will be possible.

A surface resonance has been observed on the (110) surface of tungsten using angle-resolved photoemission. The resonance is located near the center of the surface Brillouin zone in a pseudo gap opened by the spin-orbit interaction and lies at a binding energy of 1.18 eV at $\bar{\Gamma}$. It is degenerate with a bulk band which, in the absence of the spin-orbit interaction, would have a different symmetry than a state in the gap. The resultant weak coupling leads to formation of a well-defined surface resonance. This state is extremely sensitive to contamination, and is attenuated rapidly in the ambient vacuum of $0.8-1.5 \times 10^{-10}$ torr obtained in these experiments. This combined with its lack of dispersion with $k_{\perp}$ (the Σ direction) and the dependence of its intensity on photon energy confirms its identification as a surface resonance.

The Σ direction in the bulk system is composed of bands of Σ_5 symmetry in accord with double group representation. No gap exists in the binding energy range of the observed feature. In fact, the resonance lies in a "pseudogap" between the Γ_8 and Γ_7 bands at $\bar{\Gamma}$. We refer to this as a pseudogap because the only degenerate bulk band is of Σ_5^1 symmetry. The superscript in this designation refers to the symmetry of the band prior to doubling the group as required upon introduction of the spin-orbit interaction. An electronic energy level having substantially different single-group character will be coupled only weakly by the spin-orbit interaction to the Σ_5^1 continuum, and thus a well defined surface resonance may exist. We interpret the surface resonance in this context.

Support for this interpretation comes from the fact that the intensity of the surface resonance is maximized when the final state momentum probes the vicinity of the bulk band edges. This is in accord with the expectation for a surface localized state¹. In addition the polarization dependence of the intensity of the state is in accord with the expectations for a surface resonance as defined in the previous paragraph.

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Acknowledgement: USDOE grant DE-FG06-86ER45275 and Am. Chem. Soc. Petroleum Res. Fund

SURFACE STATES AND RECONSTRUCTION ON W(110)

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Surface reconstructions have been observed in a variety of metal and semiconductor systems. Adsorbate-induced reconstructions are of particular interest since this class of reconstructive behavior has direct implications for questions related to the bonding of atoms and molecules to surfaces. This is because the perturbations of the substrate electronic structure induced by adsorbate bonding are directly responsible for the geometric rearrangement of the substrate; i.e., a new ground electronic state is induced which requires a new geometric configuration. At a very fundamental level, concepts such as stress, strain, and force constant softening, which are often invoked to explain reconstruction, are determined by the electronic structure.

Most reconstructions involve an enlargement of the unit cell of the surface layer. However, Chung, et. al., have recently observed that W(110) undergoes a hydrogen-induced reconstruction which can be described as a unidirectional displacement of the top layer with respect to the second layer¹. Since the unit cell size remains unchanged, the reconstruction was detected by observing the loss of the $\bar{1}10$ mirror plane of the surface. A simple model which accounted qualitatively for this reconstruction was introduced. A translation of the first layer relative to the second indicates that the balance between first to second layer bonds projected onto the $\bar{1}10$ and 001 directions has been altered as a result of hydrogen adsorption. In the interest of characterizing such changes, we have measured the modifications of the electronic structure upon adsorbing hydrogen on both surfaces using high-resolution angle-resolved photoemission.

On clean W(110), a variety of surface electronic states were observed which had not been previously detected due to the poorer resolution available in earlier studies^{2,3}. Most of these features are exceedingly sensitive to hydrogen adsorption, being quenched by less than 0.1 monolayers. Since the W(110) surface is reconstructed only after adsorbing in excess of 0.5 monolayers, we conclude that these ultrasensitive states are not directly related to the reconstruction. The most interesting features we have observed exist in surface projected band gaps near the Fermi level (E_F) which are opened by very strong bulk band hybridization. For example, in the vicinity of $k_{||}=0.6 \text{ \AA}^{-2}$ along $\bar{\Sigma}$, two bands near the Fermi level which are nearly degenerate for the clean surface, are observed to split upon hydrogen exposure. The higher binding energy feature shifts by as much as 0.6 eV, enough to traverse the entire gap. Adsorption of oxygen destroys this feature altogether, implying that it is indeed a surface localized state. The different behavior of this band toward the two adsorbates implies that it may be related to the tendency to reconstruct, since oxygen does not induce the structural modification. More detailed studies indicate that the band forms a narrow segment of the Fermi surface near the $\bar{\Sigma}$ line which expands dramatically in the direction normal to $\bar{\Sigma}$ as hydrogen is added. In addition to the large energetic changes implied by these data, there must be significant rehybridization of the electronic levels in the vicinity of the surface: On the clean (covered) surface, the surface state will resemble the bulk states at the top (bottom) of the gap. Since the gap is opened by hybridization, these levels are quite different in their bonding/antibonding character. The observed change then presumably leads to a renormalization of the force constants near the surface, possibly to a softening of a surface phonon mode, and consequently to the reconstruction.

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Acknowledgement: USDOE grant DE-FG06-86ER45275 and Am. Chem. Soc. Petroleum Res. Fund

ELECTRONIC STRUCTURE OF C, N AND O ADSORPTION STRUCTURES ON Ni(100)

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Adsorption of oxygen on Ni(100) is well-known to produce, at a nominal half-monolayer coverage, a $c(2 \times 2)$ chemisorbed phase in which the oxygen atoms lie slightly above (0.9Å) an unreconstructed metal surface. A similar coverage of carbon or nitrogen, however, leads to the adsorbate atoms adopting almost coplanar site within the top metal layer leading to a surface metal layer distortion to accommodate these atoms with a $p(2 \times 2)p_4g$ mesh and space group[1]. In an earlier study of the surface carbide phase we compared the results of an ARUPS band mapping of the adsorbate-induced features with ARUPS from the clean surface and the results of a FLAPW calculation of the electronic structure of an unreconstructed surface structure[2]. This revealed generally good agreement for the main C 2s and 2p induced features but also indicated changes in the metal d-band region which might be involved in driving the reconstruction. Comparison of similar data for graphitic overlayers on this surface also indicated the strength of the C-C and C-Ni interaction[3].

In a new series of experiments we have extended this ARUPS band mapping to the N and O adsorption structures with the object of further clarifying the difference between the electronic structures of the reconstructed and unreconstructed surfaces. Full analysis of the data is not yet complete and further related slab calculations are also in progress. The data do show, however, that the trend in the C adsorption structure ARUPS to show the strongest C-induced features in higher surface Brillouin zones is reproduced for the N-induced structure. One particular problem in studying the Ni(100) $c(2 \times 2)$ -O structure which is widely recognised is that islands of NiO start to nucleate on the surface at average coverages below one half of a monolayer. We have therefore also collected ARUPS spectra for the higher coverage, oxide-dominated phase. These clearly allow the chemisorption features to be distinguished from those associated with surface oxide formation.

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A.L.D.K. and D.P.W. acknowledge the financial support of the Science and Engineering Research Council of the U.K. for this work.

A Preliminary Report on "Dragon" Monochromator: the Spherical Version of the Cylindrical Element Monochromator

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Tunability, high resolution and high flux in the soft x-ray region is highly demanded by spectroscopists and is a great challenge to synchrotron radiation machine physicists and monochromator designers. Monochromatization of synchrotron radiation in the photon energy 300 eV to 1000 eV range has been a very difficult task, because crystal monochromators are inapplicable and grating monochromators must work at every grazing angle (2-4 degree) and so suffer seriously from aberration and figure error of the optical elements. To meet this challenge, a new cylindrical element monochromator (CEM) design for soft x-ray synchrotron radiation has been proposed.¹ Design and construction of such a monochromator (which is dubbed "Dragon" and is the spherical version of the CEM design) has been carried out in its entirety in the period October 1985 to July 1987. During the UV-ring 1986 fall shutdown, the existing U4 PGM was removed and the installation of Dragon was started. On July 13, 1987, Dragon delivered its first monochromatized photon beam.

Figure 1 displays the conceptual layout of the CEM design. At the left of the figure there are two mirrors, the one closer to the source is the horizontal focusing mirror (HFM), and the other is the vertical focusing mirror (VFM). These two mirrors are close to each other and each one focuses in only one direction. Therefore the optical functions are decoupled. The top view shows the HFM focusing the source inside the storage ring onto the sample position while the side view shows the VFM focusing the source into the entrance slit. Behind the entrance slit, the grating diffracts and focuses the beam vertically into the exit slit. The wavelength scanning mechanism is a simple sine-drive for the grating and a linear stage for the exit slit. The coupling between these two motions is not demanding, because the tolerance of the exit slit position for a given grating scanning angle is few centimeters. Although the ideal surface figure for all these optical elements is elliptic cylinder, the replacement by circular cylinder or even sphere will not degrade the CEM performance.¹

Recently, we have utilized the Ca $L_{2,3}$ and F K absorption edges of CaF_2 crystal to align and characterize the Dragon monochromator. Figure 2 shows a set of spectra with both slits set at 10 μm and angular acceptance set at 12 mrd $\times$ 1 mrd. The 0.25 eV and 0.66 eV FWHM measured in peaks at photon energies 351 eV and 688 eV respectively, demonstrate the resolving power of the Dragon (better than 10^3). The ultimate monochromator resolution as well as photon flux of the Dragon will be exploited in the near future.

Various ideas of the CEM design, which contain important advantages over existing soft x-ray monochromators, have been realized in the Dragon monochromator. They include: (1) Promise of high resolution and high transmission. (2) Energy resolution being independent of horizontal angular acceptance. (3) Movable exit slit eliminating defocal aberration. (4) HFM serving as a heat and radiation protector for the VFM and the grating. (5) Due to the decoupled nature, the whole beamline being easy to align and operate. Further commissioning and studies are in progress in order to reach the ultimate performance.

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Fig. 1. Conceptual layout of the cylindrical element monochromator design.

Fig. 2. Ca $L_{2,3}$ and F K edge absorption spectra of CaF_2 crystal taken with the Dragon monochromator with 10 μm - 10 μm slits and 12 mrd $\times$ 1 mrd angular acceptance.

THE INFRA-RED BEAM LINE IR4

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During the last year, the infra-red beamline front end components were installed. Mirrors 1-5 were installed and aligned, thus enabling the beam to be transported to the secondary focus at a quartz window. The latter is located on a platform above the VUV floor.

The beamline was first opened to the ring, and first light extracted on May 4th, 1987. Since that time, most of the components shown in the figure, which is a plan view of the platform layout, have been installed.

In July the first spectrum was measured using the Michelson interferometer. This instrument allows the NSLS to be compared with a black-body source. Using a quartz window, at a wavelength of 100 microns, (100 wave numbers or 10meV), the NSLS at 500m amps was found to be around 500 times brighter than the black body source. This result agrees well with theoretical predictions. Immediate plans call for the installation of the diamond window. Careful NSLS source characterization measurements will then be made.

NSLS INFRA-RED BEAMLINE
BEAMLINE LAYOUT

PHOTOEMISSION STUDIES OF THE HIGH T_c SUPERCONDUCTOR $YBa_2Cu_3O_{9-\delta}$

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We have recorded photoemission spectra from the high T_c superconductor $YBa_2Cu_3O_7$ as a function of photon energy. The samples were cleaned by scraping the surface under UHV conditions. By examining the spectra as a function of photon energy it was possible to determine the copper and oxygen components in the density of states from their different cross-sectional behavior. Thus at low energies one observes emission from both the copper and oxygen components whereas at higher energies the density of states is dominated by emission from the copper 3d states. It was further observed that at the Fermi level the measured density of states was extremely low.

In Fig. 1 we show a comparison of our measured density of states with a theoretical calculation due to Mattheiss and Hamann.^[1] It will be seen that both components in the experimental spectrum, copper at 4.3 eV and oxygen at 2.3 eV with respect to the Fermi level, are shifted to higher binding energies when compared with the theoretical calculation. The origin of this shift probably reflects in part the presence of the photo hole and in part the fact that the calculation employs the local density approximation (LDA). It is well established that LDA tends to underestimate the binding energy of more localised orbitals.

Finally we note that the experiment was carried out on a liquid helium cryostat. Measurements above and below T_c showed no change in the spectra.

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Fig. 1. Comparison of the measured density of states with the calculated density of states from Matthesis and Hamann (Ref. 1).

DEGRADATION OF POLY(METHYL METHACRYLATE) BY X-RAYS

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Poly(methyl methacrylate) PMMA, widely used as an electron beam resist, has also been used as an X-ray resist. An inherent part of the lithographic process in the fabrication of microcircuits is the degradation of PMMA caused by deep UV, X-ray, electron beam or ion beam irradiation. The enhanced dissolution rate resulting from this degradation permits images to be developed in polymer films. The purpose of this effort was to study the degradation mechanism of PMMA caused by synchrotron X-rays and to compare the results with UV, e-beam and ion beam irradiations. PMMA undergoes loss of ester side groups and scission of the main chain as a result of irradiation.

In this work, Fourier transform infrared (FTIR) difference spectrometry and UV difference spectrometry are used to measure directly the changes in PMMA films upon X-ray irradiation. The observed changes are related to the decrease of specific functional groups and to the generation of new functional groups.

The decrease of the carbonyl ($C=O$) stretching band at 1730 cm^{-1} was found to be proportional to the incident dose of X-rays. The increase of the 195 nm absorption (caused by generation of $C=C$) in the UV spectrum was also proportional to the incident dose. The number of main chain scissions of PMMA was similarly proportional to the incident dose.

The removal of ester groups was calculated from the FTIR difference spectrum using standard and well known procedures relating absorbance, film thickness and concentration.

The number of $C=C$ bonds generated was close to the number $C=O$ groups removed by X-irradiation to a dose of 1 J/cm^2 . In other words each removal of an ester group generates $C=C$ bond by main chain scission or abstraction of hydrogen from the main chain.

The ratio of main chain scission to the change of specific functional groups depends on the type of radiation. Table 1 shows a comparison of the results obtained with different radiations. It is apparent that the X-rays were the best at causing main chain scission with high efficiency and less removal of ester groups.

Table 1

Degradation of Poly(methyl methacrylate) by UV, E-beam, X-ray and Proton beam (main chain scission, ester group removal and carbon carbon double bond generation per 100 monomer units in PMMA).

	DUV 4 ~ 6 eV 0.6 J/cm ²	E-Beam 25 KeV 20 $\mu\text{C/cm}^2$ (0.5 J/cm ²)	X-Ray 0.8 ~ 1.8 KeV 1 J/cm ²	Proton-Beam 300 KeV 1 $\times 10^{13}\text{ H/cm}^2$ (0.48 J/cm ²)
Main Chain Scission (MCS)	0.22	0.46	1.08	0.75
Ester Removal ($C=O$)	8.53	2.59	3.68	3.22
Ratio $\frac{\text{MCS}}{C=O}$	0.026	0.178	0.293	0.233
$C=C$ generation ($C=C$)	7.06	2.24	3.72	2.83
Ratio $\frac{\text{MCS}}{C=C}$	0.031	0.205	0.290	0.265

EFFECTS OF X-RAY RADIATION ON THE PHYSICAL PROPERTIES OF BORO-HYDRO-NITRIDE FILMS

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The effects of X-ray radiation on the physical properties of Low Pressure Chemical Vapor Deposited "boro-hydro-nitride" films¹ have been studied using "white light" synchrotron radiation at the U-6 beamline at the National Synchrotron Light Source. The purpose of this study was to shed some light on the mask radiation damage, an issue of great importance and concern in X-ray lithography. Radiation effects relevant to X-ray lithography include mechanical distortion and optical darkening of mask membranes prepared from such films.

Our results indicate that such films show a reduction in optical transparency on the order of 10% for an incident dose of 700 J/cm², with no significant additional reduction occurring when exposed to an additional 400 J/cm². Following irradiation, the boron to nitrogen ratio and hydrogen content were analyzed respectively by electron microprobe and resonant nuclear reaction techniques; no change in chemical composition upon irradiation was detected.

The DC electrical resistivity of LPCVD boro-hydro-nitride films was measured for various film deposition parameters and found to be directly related to both the optical transparency and the mechanical stress of the x-ray mask membranes prepared from these films. The influence of the film's hydrogen and boron content on electrical resistivity is also being reported. The electrical resistivity was observed to decrease after irradiation, as shown in Fig. 1 for successive exposures, for various values of the deposition parameter R, which is the incident gas ratio of ammonia to diborane. The rate of change of the electrical resistivity with dose increases with the film's initial (measured before irradiation) resistivity. Experimental results (shown in Fig. 2) suggest that the radiation damage relevant to x-ray lithography in the mask membranes is directly related to their initial electrical resistivity and is most pronounced for films with the highest as-deposited initial resistivity.

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Fig. 1. Effect of radiation on films deposited under different conditions (at 400°C)

Fig. 2. Optical damage as a function of initial film resistivity after exposure to 1100 J/cm²

Mn OVERLAYERS ON Ru(001) SURFACE

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Manganese overlayers have interesting chemisorption properties¹ and Mn metal is used as a catalyst in several industrial processes; little is known about the electronic and geometric structure of Mn promoted systems.

We have studied the valence band of the Mn/Ru(001) system using several photon energies at fixed sample geometry. Synchrotron experiment confirmed previous results² obtained with HeI photons, namely, that the pseudomorphic Mn layer has a valence band similar to that of clean Ru even for the multilayer coverages. Using various photon energies we can conclude that the peaks in the spectra of Fig. 1 are due to initial states.

Carbon monoxide adsorbed on a pseudomorphic Mn layer shows typical 4σ and $5\sigma/\pi$ orbitals. The shape, intensity and position of CO derived peaks are identical to what is observed for CO adsorbed on a Ru(001) surface. This observation is paradoxical in view of complementary surface experiment carried out on the same system¹: CO bonding should be severely perturbed on the Mn layer. We will investigate the system in greater detail with synchrotron radiation in the near future.

Pseudomorphic Mn overlayer on Ru is in an expanded lattice and magnetic properties of such a system were studied recently.³ In Fig. 2 we show that the splitting of the Mn 3s core level of pseudomorphic (1 and 2 ML) Mn overlayers is 5.7 eV. Such a large splitting is typical for Mn with magnetic moment close to $5 \mu_B$. For thicker Mn layers (5 and 10 ML) the Mn 3s peaks broaden and shift to higher binding energy. A possible explanation is the presence of Mn atoms in nonequivalent positions in the lattice.

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Fig. 1. Valence band spectra of pseudomorphic Mn.

Fig. 2. 3s splitting in Mn overlayer.

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.

Cu{001}c(2x2)-Pd: a surface alloy **atomic arrangement and electronic structure**

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There is, to date, only one reported case of surface-alloy formation that was quantitatively proven and adequately documented by both experimental^{1,2} and theoretical³ studies — the case of Cu{001}c(2x2)-Au. A second case, reported here, is the one obtained from the room-temperature reaction of a clean Cu{001} surface with less than one monolayer of Pd. The resulting phase is an ordered c(2x2) layer, denoted Cu{001}c(2x2)-Pd. We summarize here the results of LEED and UPS studies of this phase.

The LEED study involved a quantitative intensity analysis of data collected both at normal and off-normal incidence. Four independent sets of intensity data were used, including a total of 26 beams at normal and 22 beams at non-normal incidence. The analysis showed that the top atomic layer was a *mixed* layer in which every other Cu atom had been replaced by a Pd atom, with no ordered Pd content beyond the first layer, which is what we call a surface alloy. The mixed layer is almost planar, with the Pd atoms only slightly outward of the Cu atoms by 0.02±0.03 Å (in contrast to the Au-Cu surface alloy, which is markedly buckled¹). High background in the LEED pattern of the Pd-Cu phase suggested that some Pd atoms may possibly reside either above or below the first layer, although not with long-range order. This possibility is further supported by the fact that the "best" LEED patterns (sharp spots and high contrast) were consistently observed only after deposition of 0.7-0.8 monolayer equivalents of Pd (ideally, only 0.5 monolayer-equivalents are required to form a perfect c(2x2) structure). Nevertheless, the LEED analysis established unambiguously that the predominantly ordered product of the Cu-Pd reaction was indeed a surface alloy.

The UPS study, carried out on beamline U7B with photon energies varying between 12.5 and 130 eV, confirmed the alloy character of the surface phase and revealed an interesting splitting of the Pd *d* states. We show in the figure, as an example, the valence bands (after background subtraction) of clean Cu{001} (dashed), of clean Pd{001} (dash-dotted) and of the Cu{001}c(2x2)-Pd surface alloy (solid). In the latter spectrum we identify the features at -1.7 and -4.8 eV with Pd-derived bands and the peak at -3.0 eV with the Cu-derived band. This assignment stems from a series of observations. Electron distribution curves (EDC) obtained with photon energies ranging from 12.5 to 130 eV showed that, while the intensities of the Pd-derived peaks varied substantially with photon energy, their energy dispersion was almost nil. The intensity and the dispersion of the Cu-derived feature resembled closely those of clean Cu{001}, except for a shift of about 0.4 eV toward larger binding energy. At a photon energy of 130 eV, where the photoionization cross section of Pd is a minimum, the EDC of Cu{001}c(2x2)-Pd was equal to that of Cu{001} except for a shift of about 0.6 eV toward lower binding energies. Thus, the spectra of the surface alloy are characterized by the presence of two well-separated Pd-derived bands about 3.1 eV apart. This phenomenon was observed before on single crystals of *bulk* Cu-rich Cu-Pd alloys and was confirmed theoretically by calculations of complex-energy bands and average densities of states by Rao *et al.*⁴ The calculated positions of the Pd-derived features are shown with arrows in the figure. Physically, the phenomenon has its origin in the large-crystal-field splitting associated with the Pd muffin tin potential in the alloy, and also in the particular circumstance that the Cu *d* band lies roughly in the middle of the substantially broader Pd *d* band. The Pd *d* states then tend to get excluded from the middle region and give rise to a two-peaked structure in the density of states on the Pd site. Thus, the UPS results are consistent with the LEED results in confirming the alloy nature of the surface phase and in showing that the Pd-derived features behave indeed like surface states.

This work was sponsored in part by the Department of Energy with Grant DE-FG02-86ER45239A001.

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STUDIES OF POTASSIUM WITH SOLID AMMONIA

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Alkali metal-ammonia solutions are model systems for studying Metal-Nonmetal transitions and potassium is of particular interest since it plays a catalytic role in the process of producing ammonia. We have studied this system by depositing different thicknesses of potassium on a Ta substrate and then condensing solid ammonia on the surface of the sample at liquid nitrogen temperature. The first spectrum at the bottom of Fig. 1 shows the 3p core level characteristic of metallic K (~18 eV), and the 4f levels of Ta (~22-25 eV). The thickness of K in Fig. 1 is 0.76 ML. At 0.2 ML coverage of NH₃, a high binding energy feature of the 3p core level of K shows up and the intensity of this feature increases with increasing NH₃ coverage. We have previously shown in studies of Na on solid ammonia that this high binding energy feature is due to non-metallic or "solvated alkali metal". For a smaller K coverage of (0.23 ML) there is no such high binding energy feature at any coverage of NH₃. We interpret this to mean that the K does not solvate in the solid ammonia in this case. We have also deposited K on a thick layer (about 30 Å) of solid NH₃ (Fig. 3). At low K coverage, only the high binding energy feature of the 3p core level appears, but at a certain coverage of K, the metallic 3p peak 10¹⁵ starts to develop as in the case of Na on solid ammonia^[1]. This is possibly related to the Metal-Nonmetal transition or the formation of large metal clusters. At high coverage of K (about 5.6 x 10⁻¹⁵ atoms/cm²) the metallic 3p peak dominates while the high binding energy feature becomes a shoulder. At this point by condensing solid ammonia on the top of K, the inverse process can be seen, as shown in Fig. 3 (the top three spectra). With increasing exposure of NH₃ the intensity of the high binding energy feature increases, and finally the metallic peak disappears and the high binding energy feature dominates.

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Fig.1 Solid ammonia on potassium (0.76 ML). At 0.2 ML coverage of NH₃ the feature of the "solvated potassium" appears.

Fig.2 Solid ammonia on potassium (0.23 ML). There is no the feature of the "solvated potassium" at any coverage of NH₃.

Fig.3 The change from the "solvated K" to the "metallic K" and its inverse process.

GROWTH OF Yb FILMS ON Ta

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We have studied the growth of Yb films on a recrystallized Ta(110) surface with photoemission. From the electron energy distribution curves (EDCs) of the core levels and the valence band, we find that the Yb appears to grow layer-by-layer for the first two to three layers. Representative valence band spectra can be seen in Fig. 1 and core level spectra can be seen in Fig. 2. All the sites occupied by the Yb initially are equivalent as seen from the Yb 4f and 5p core level peaks measured. In the submonolayer regime, Yb is divalent as is the case for Yb atoms on the surface of Yb metal or compounds including intermetallic compounds where the Yb in the bulk may be mixed valent or trivalent. The Yb 4f peaks and the 5p peaks are uniformly shifted towards lower binding energy than those of Yb atoms on an Yb substrate suggesting that the Ta substrate provides more effective screening for the emitted electrons. Another effect of the Yb layer is to reduce the width of the Ta 4f_{7/2} peak; an indication that the Ta surface shifted peak has been eliminated due to screening provided by the Yb. As the amount of Yb is increased further so that the second layer of Yb begins to grow, the outermost Yb layer sees an Yb substrate giving a doublet of 4f emission whose position is consistent with surface Yb atoms on an Yb substrate. The emission from the Yb at the Yb-Ta interface shifts to lower binding energy with the addition of a second layer of Yb due to fewer "dangling" bonds. This is also reflected in the Yb 5p emission where one sees two peaks due to 5p_{3/2} emission. These can be seen more clearly on subtraction of the Ta contribution to the signal. With the evaporation of enough Yb, bulk Yb spectra are recovered.

Fig.1 Valence band of Yb on Ta.

Fig. 2 Core levels of Yb 5p and Ta 4f as a function of the coverage of Yb.

Work supported by the Division of Materials Sciences U. S. Department of Energy under Contract No. DE-AC02-76CH00016

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THE NATURE OF THE INTERFACE FOR Pd OVERLAYERS ON Ta

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The properties of bimetallic systems are of great interest for obtaining surfaces with greatly modified properties. Pd on Nb or Ta is such a case where there is a considerable modification of the properties of the Pd overlayers. The overlayer system has been made in two different ways. First, by depositing a monolayer of Pd on Ta and second by depositing a thick Pd layer then heating to 800°C in which case only about one monolayer remains on the surface. In both cases the LEED pattern indicates that the Pd "layer" has the Ta(110) structure, and the electronic properties show that the d bands are similar in these two cases and are significantly below E_f , when compared to opposed to bulk Pd. In this work, we have studied the behavior Ta 4f level to see if the Pd*(110) overlayers made by these different methods are actually the same. In Fig. 1, the development of the interface compound is studied as Pd is deposited without heating. The first spectrum from the bottom shows the clean bulk Ta 4f levels, and upward from the second spectrum the evolution as a function of Pd coverage of the shifted feature due to bonding at the interface is seen. At about one monolayer of Pd, the intensity of the interface feature becomes comparable to that of the bulk Ta 4f feature. Above monolayer coverage, the intensities of both features decrease with increasing Pd coverage. Figure 2 shows the development of the interface compound produced by heating a thick layer of Pd on Ta. From about 700 to 900°C the compound is stable, and at 800°C the shifted feature was heated for one hour and no change in the compound was observed. It is also seen that the interface feature is significantly higher than the bulk Ta feature, which indicates that the interface must extend over several layers. Apparently the configuration formed by depositing a monolayer of Pd is not equivalent to that formed by heating a thick Pd layer; even though the LEED patterns and the chemical properties of the layers are similar. This system will be looked at again with higher resolution on the U7A TGM.

Fig.1 The interface compound of Pd/Ta as a function of the coverage of Pd. The Ta 4f levels were used as a probe.

Fig.2 The evolution of the interface compound by heating a thick layer of Pd on Ta. The Ta 4f levels were used as a probe.

Work supported by the Division of Materials Sciences U. S. Department of Energy under Contract No. DE-AC02-76CH00016.

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RESONANT AND X-RAY PHOTOEMISSION STUDIES OF THE $\text{YBa}_2\text{Cu}_3\text{O}_7$ VALENCE BAND
ABOVE AND BELOW THE SUPERCONDUCTING TRANSITION TEMPERATURE

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A description of the electronic structure of high T_c superconductors is essential, if an understanding of the superconducting mechanism is to be achieved. A number of theoretical models have been advanced to explain the high transition temperatures. Some of these models invoke charge fluctuations on the Cu ions between a 2^+ and 3^+ state. Other models suggest that holes become localized on the oxygen O^{2-} ions. Resonant valence band photoemission spectra and photoemission core level spectra along with other complimentary techniques should be able to detect changes in the charge state of Y, Ba, Cu or O ions and show changes in the degree of screening of the photon produced holes. Photoemission spectra from freshly scraped surfaces at room temperature (300°K) and for surfaces scraped at room temperature but cooled to 20 K for the superconducting compound, $\text{YBa}_2\text{Cu}_3\text{O}_7$ using photon energies ranging from 50 to 150 eV. Valence band spectra (Fig. 1) for room temperature $\text{YBa}_2\text{Cu}_3\text{O}_7$ shows resonant photoemission which permits the identification of the chemical origin of the peaks in the valence region, an extremely low density of states at the Fermi level and a $\text{Cu}3d$ satellite (about 13 eV binding energy) seen near the 74 eV $\text{Cu}3p$ photoadsorption threshold. The appearance of this satellite in the spectra is consistent with a Cu^{2+} valence. In spectra, recorded at temperatures below T_c , photoemission from the $\text{Cu}3d$ satellite becomes less intense suggesting possible electron delocalization. Otherwise the valence band shows little or no change between 300 and 20 K. A conventional x-ray source was attached to the U7-B experimental chamber to permit studies of the valence charge state in the surface layer by XPS. Examination of the $\text{Cu } 2p_{3/2}, 2p_{1/2}$ core level (Fig. 2) suggests that the copper valence is 2^+ because the poorly screened "satellite" peak, seen in CuO , is present. The O 1s (Fig. 2) show principle components at 529 and 531 eV binding energy and a much weaker component at 533 eV. Observation of several oxygen species suggests that the surface layer is multi-phase in regards to oxygen concentration or suggests that significant impurity phases (e.g., BaCO_3 or $\text{Ba}(\text{OH})_2$) may be present. Like the valence band, the core level spectra show little change in either binding energy or shape upon cooling below the superconducting transition temperature. This also suggests little or no change occurs in the chemical state of the surface layer, or in the screening of the final state hole.

Fig. 1. Valence band spectra

Fig. 2. Corelevel spectra

Work supported by the Division of Materials Sciences U. S. Department of Energy under Contract No. DE-AC02-CH00016.

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INTERACTION OF OXYGEN WITH A HIGH T_c SUPERCONDUCTING OXIDE AT LOW TEMPERATURE

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Molecular oxygen was adsorbed on a freshly scraped $YBa_2Cu_3O_7$ surface and its interaction with the substrate was probed using synchrotron radiation and x-ray photoemission. No significant amount of oxygen appeared to absorb at 300°K and subsequent gas exposures were performed on a surface cooled to 20°K. Valence band spectra (Fig. 1a) taken at 150 eV show additional photoemission peaks (Fig. 1b) characteristic of physisorbed molecular oxygen after several small exposures. O 1s core level spectra also show a peak at 538 eV characteristic of molecular oxygen. An additional peak at 533 eV is observed to grow with increasing oxygen exposure. Reduction in surface O_2 coverage occurs and might be attributed to either gradual desorption or diffusion into the bulk. The physisorbed oxygen could be removed by warming the sample to 50°K. At this temperature the 538 eV O 1s feature disappears, but the 533 peak retains its intensity. The valence band shows radical changes when compared to either the spectrum taken at 20°K with no oxygen adsorbed or a spectrum taken at room temperature. Intense new valence band states are seen near -7, -12, and -27 eV binding energy. The valence band spectrum reverts to the room temperature spectrum when heated above 200°K. Examination of Ba, Y or Cu core levels indicates little modification of the electronic structure. Reversion of the valence band back to its initial configuration suggests that the underlying atomic structure is unchanged and that additional physisorbed oxygen causes little chemical break down of the material. The nature of the modified valence band and its connection with surface layer oxygen concentration is under investigation.

Fig. 1(a). Valence band spectra taken using 150 eV photons
1(b). O 1s core level spectra taken using Al K- α x-rays

Work supported by the Division of Materials Sciences U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

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FORMATION OF Al/Ta(110) INTERFACES AND THEIR MODIFICATION BY OXIDATION

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Interactions between Al and a refractory metal were examined to gain insight into the chemical and physical processes important in making sapphire-Nb thin film superconducting devices. To facilitate the experiment, Ta was substituted for Nb and junctions between Al and Ta were made by vapor deposition of Al on a Ta substrate in ultrahigh vacuum ($\sim 5 \times 10^{-10}$ Torr). No evidence of intermixing between Al and Ta below 1 nm thickness was detected and intensity variation of the Ta 4f core level suggests that Al initially goes down layer-by-layer. Possible clustering and surface roughening are detected for Al coverages exceeding 1 nm. No shifted Ta 4f core level component is seen but modification of the Ta valence band suggests that sufficient bonding to account for the formation of a uniform flat Al overlayer at monolayer coverages exists. Heat treatments ($\sim 700^\circ\text{C}$) trigger interdiffusion and reaction to form a stable Ta-Al intermetallic compound. Further mixing of Ta and Al did not occur until temperatures exceeded 900°C and small amounts of Al were present at 1100 – 1200°C . The observation of Al on the surface at these high temperatures suggests that the surface Al-Ta bond is stronger than the Al-Al bond. We have also studied the oxidation of one and two monolayers of Al on Ta to see how the oxide develops at the Al-Ta interface. One pronounced feature is the enormous increase in the number of Langmuirs of oxygen exposure necessary for the formation of the Ta_2O_3 features (about 1 eV deeper than the main 4f peaks) with increasing thickness of Al film. For clean Ta about 1L oxygen exposure shows well developed features, whereas for one layer of Al similar features are seen at about 20–50 L exposure and for two layers of Al these features are seen above 1000L exposure. The 5 eV deeper peaks of Ta_2O_3 are seen at above 500L for clean Ta, at about 5000–50000L for one layer of Al, and there is no indication of this oxide for 2 layers of Al at an exposure of 50000L. Figure 1a shows the features of Al 2P core level as a function of the oxygen exposure for one layer of Al. The feature at -1.4 eV relative to the clean peak shifts to high binding energy with increasing oxygen exposure and stays at -2.6 eV after 500L oxygen exposure. For two layers of Al (Fig. 1b) at about 50L oxygen exposure the feature of bulk Al_2O_3 at -2.6 eV starts to develop and shifts to -3.2 eV with increasing the oxygen exposure, while after 5000L it shifts back to -2.6 eV. This can be interpreted as the formation of the Ta_2O_3 layer underneath which causes the shift of the substrate vacuum level.

Fig. 1(a). Oxygen on a Al/Ta(110) monolayer
1(b). Oxygen on two Al layers supported on Ta(110)

Work supported by the Division of Materials Sciences U. S. Department of Energy under Contract No. DE-AC02-76CH00016.

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ROOM TEMPERATURE INTERMIXING AT Cu-Al INTERFACES

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Synchrotron radiation photoemission was used to study room temperature interface formation between Cu and Al. The experiment observed small scale (1-2 nm) intermixing at 300 K for both Cu/Al and the inverted Al/Cu junctions. The Cu or Al films were deposited on an inert substrate in ultrahigh vacuum to minimize impurities in the thin films or at the interface. 60 eV photoemission spectra for the Cu-Al are shown in Fig. 1(a). Modification of the Cu 3d-states suggests that Cu and Al have either alloyed or intermixed. Clustering of the Cu film can be ruled out because the "atomic-like" Cu states are observed even after five Cu monolayers are deposited. Slow attenuation of the Al 2p core level during the early states of Al overlayer formation is consistent with significant surface alloying. More rapid attenuation of the Al 2p core level seen at later stages of interface formation can be explained by the burial of the extended interface by metallic Cu. Comparable intermixing is also seen for Al-Cu because the high Al coverage spectra show Cu photoemission features suggestive of the presence of an atomic-like Cu species Fig. 1(b).

Fig. 1. 60 eV valence band photoemission spectra for the Cu-Al and Al-Cu interfaces, θ is the overlayer coverage in monolayers

MORPHOLOGY, BONDING AND THERMAL STABILITY OF Cu/Ta(110) Au/Ta(110) OVERLAYERS

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The structure, electronic properties and thermal modification of Cu/Ta(110) and Au/Ta(110) were studied using synchrotron radiation photoemission. The linearity of the attenuation curve of the Ta 4f core level, Fig. 1(a) indicates that the growth of Cu on Ta(110) occurs in a layer-by-layer fashion. From LEED data and similar attenuation trends for the Ta 4f core level, it is also concluded the Au overlayers undergo epitaxial layer-by-layer growth. Modifications of the Au valence band states and core level binding energy shifts for both the Au 4f and Ta 4f states suggest that some bonding occurs between Au and Ta. However, the lack of change in the Ta d-band states or Au-d states when observed near the Cooper minimum for Au suggests little direct involvement of the Au metal d-states in forming bonds. A shift to lower binding energy (i.e., towards the metallic Au position) by the Au 4f level occurs near the coverage required to cause the Au overlayer to revert to the close packed fcc structure. For Cu/Ta(110), (Fig. 2) "atomic-like" Cu states can be seen below 2 monolayers (ML) Cu. Metallic Cu states are evident after 4 ML. No shift of the Ta 4f core level is seen when Cu is deposited. This suggests that the bonding between Cu and Ta is less than that which occurs between Au and Ta. A thick layer of Cu was heated up to 900°C. The relative intensity of Ta 4f core level versus temperature is shown in Fig. 1(b). During this process no shifted Ta 4f core level is observed and the valence band states of Cu shifted to the "atomic-like" position and this suggests that the interaction between Cu and Ta is small. The data for Cu/Ta(110) is consistent with thermally induced clustering. Heating above 800°C triggers significant mixing of Au and Ta which leads to the formation of a stable surface compound. The lack of a bulk metallic Ta 4f core level component suggests that the intermixed Au-Ta layer is thicker than the probing depth of the photoelectrons. Changes in the Au valence band and binding energy shifts of the Au and Ta core levels are similar to those seen for chemisorbed Au/Ta(110). Further heating, in excess of 1000°C destroys the Au/Ta surface and recovers the clean Ta surface.

Fig. 1. Ta 4f corelevel intensities for Cu/Ta(110)

Fig. 2. EDCs for Cu/Ta(110) films

Work supported by the Division of Materials Sciences U. S. Department of Energy under Contract No. DE-AC02-76CH00016.

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Microscopic Structure of the SiO₂ / Si Interface

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A variety of techniques has been used to study the structure of the SiO₂/Si interface. The high electronic quality of this interface is the key to today's silicon technology. Many models have been proposed for the atomic arrangement at the interface. In a previous study⁽¹⁾, we ruled out atomically abrupt models. Such models would predict only one intermediate oxidation state, i.e. Si²⁺, for the SiO₂/Si(100) interface, whereas all three intermediate oxidation states (i.e. Si¹⁺, Si²⁺, Si³⁺) are observed (see Fig. 1). In this work⁽²⁾, we propose a structural model (Fig. 2) which gives the correct intensity and distribution of oxidation states. The interfaces of Si(100) and Si(111) with SiO₂ are studied for a wide range of preparation conditions including high pressure reactions as used in device processing. As an example, we show the effect of hydrogen annealing (1 atmosphere, 1 min at 850°C). Annealing the SiO₂/Si interface in H₂ is known to reduce the density of interface states. Essentially, the hydrogen saturates free Si bonds (P_b centers⁽³⁾) at the interface. There is no detectable influence of H₂ annealing on the distribution of oxidation states. This is understandable since the number of P_b centers reaches at most about 10¹² cm⁻², i.e. 1/1000 of a monolayer. Such small changes are not detectable with our technique. However, we do see an effect of H₂ annealing on the electrical properties. The Fermi level moves to an unpinned position, which confirms the removal of interface states by hydrogen. This Fermi level movement shows up as an overall shift of the core level spectrum in Fig. 1. The shift reverses after annealing in vacuum, whereby the H is driven out.

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Figure 1. Structural model for the SiO₂/Si(001) interface derived from core level spectroscopy. The amorphous SiO₂ network (not shown) connects to the broken bonds.

Figure 2. Distribution of oxidation states at the SiO₂/Si(100) interface. Annealing in hydrogen does not change the distribution but moves the Fermi level to an unpinned position.

INTERFACE STATES AND SCHOTTKY BEHAVIOR

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The role of interface states on the electronic Schottky barrier has now been recognized. However, the origin of these states as well as their density are still controversial. Metal induced gap states¹ and/or defects² and impurities^{3,4} have often been implicated. The role of the metal, or more specifically its metallic character received⁵ but scant attention; in particular, only its role in altering the net interface charge was considered.

We set out to investigate the effect of the metal by exposing the clean cleaved GaAs surface to two different metals. The first metal, a reactive one, V or Pd was used to generate interface states of varying densities and energetic positions in the gap. The second metal a non-reactive one, Ag, was then deposited to thicknesses as high as 30 Å to monitor the effects of metallic behavior. The band bending shifts as a function of Ag coverage for various thicknesses of V interlayers are shown in fig. 1-a and 1-b. Our results show that the Fermi level approaches the valence band edge closer than either of the two metals alone. These observations are interpreted as being predominantly the effect of metallic screening.⁵

The experiments were performed at the U8 beamline, we acknowledge the technical assistance of M.Prikas and D.Costas and the co-operation of the NSLS staff.

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Figure 1. The evolution of the position of the Fermi level at the interface of GaAs with Ag coverage for various V interlayer thicknesses on n-type (a) and p-type GaAs (b). The insert shows a Ga-3d core level spectrum for a surface exposed to ≈ 0.02 ML V and covered with 3 Å Ag; the dots are the experimental points and the solid line is the sum of the bulk substrate component (dashed curve) which is used to monitor band bending shifts, the surface component (dotted curve on the low kinetic energy side) and a third component on the high KE side which is due to metallic Ga which has been replaced by V.

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The chemical state of the $\text{MoS}_2(0001)$ surface after bombardment with low-energy, noble-gas ions was analyzed by high-resolution core-level and valence-band photoelectron spectroscopies (CLPS and VBPS, respectively) on beam line U8-B. All samples were naturally occurring molybdenite crystals that were initially prepared by cleavage in air. The samples were mounted in vacuum, after which they were resistively heated to $>550^\circ\text{C}$. That treatment produced a (1×1) low-energy electron diffraction (LEED) pattern; no evidence of carbon, oxygen, or other contaminants was detected by CLPS. $\text{MoS}_2(0001)$ surfaces were bombarded with varying dosages of neon and argon ions with an energy of 1 keV.

Curve fitting of the Mo-3d doublet clearly indicates the formation of molybdenum metal after bombardment. Whereas previous studies¹⁻⁴ concluded molybdenum-metal formation on the basis of indirect information, the superior resolution (~ 0.35 eV) in this study enables the contribution of the Mo(IV) in the MoS_2 to be separated from that of the metallic Mo (see Fig. 1b). The metallic contribution increases with ion dosage until, at a dosage of $2 \times 10^{16} \text{ cm}^{-2} \text{ Ne}^+$, 85% of the surface Mo (i.e., in the top ~ 15 Å) is in metallic form (see Fig. 1c). After annealing the bombarded sample to $\sim 700^\circ\text{C}$, no LEED pattern was observed. The Mo(IV) and metallic Mo peaks of the Mo-3d spectra shifted farther apart in binding energy (see Fig. 1d). This observation, in addition to the lack of change of the peaks' relative heights as the photon energy is changed, suggests the existence, after annealing, of unconnected Mo metal islands on the surface that are thicker than ~ 15 Å.

Fig. 1. CLPS of the Mo-3d doublet for (a) the clean $\text{MoS}_2(0001)$ surface, and after 1 keV Ne ion dosages of (b) $5 \times 10^{15} \text{ cm}^{-2}$ and (c) $2 \times 10^{16} \text{ cm}^{-2}$, and (d) after subsequent annealing. A photon energy of 300 eV was used.

Extensive chemical modification is also exhibited by the sulfur in the bombarded-surface region. Curve fitting of the S-2p doublet (not shown) after ion bombardment indicates the presence of elemental sulfur in addition to a surface MoS_2 sulfur species shifted to lower binding energy as a result of sulfur vacancy formation at the surface.

Finally, VBPS of $\text{MoS}_2(0001)$ during bombardment (not shown) revealed movement of the Fermi level consistent with metallic character at the surface. Also, changes in the relative heights of the valence band peaks imply that sulfur vacancy formation during bombardment causes a decrease of the electron density in the Mo-4d areas of the valence band.

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¹This work was supported by the Air Force Space Division under contract number FO4701-85-C-0086-P00016 and by DOE, Dept. of Materials Science.

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INTERACTION OF PYROLIZED HEXAFLUOROAZOMETHANE WITH SI (111)

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One of the more interesting and important aspects of the halocarbon-based plasma etching of silicon is the control of chemical specificity. In practice, specificity in the SiO_2/Si system can be achieved by the addition of hydrogen or oxygen to a CF_4 plasma. These additions react with the plasma species to alter the nature of the reactants incident upon the substrate surface. Oxygen increases the density of free fluorine atoms in the plasma, and favors the etching of silicon. Hydrogen, on the contrary, reacts with free fluorine atoms in the discharge to produce HF, thus producing a fluorine deficient distribution of reactants and altering the relative etching rates so as to favor the etching of SiO_2 . On this basis it has been suggested that while fluorine atoms are the primary etchants for Si, CF_x species ($x=1,3$) are responsible for SiO_2 etching.

If this hypothesis is correct, the understanding of the microscopic mechanism for chemical selectivity in the SiO_2/Si system can be gained only by understanding the reactivities of each of the CF_x molecules with Si and SiO_2 surfaces. Experimentally this is a daunting task. As a possible answer to this problem, we report in this paper experiments on the interaction between clean Si (111) surfaces and hexafluoroazomethane (HFAM). The virtue of this molecule is revealed by the pyrolysis reaction:¹

The only significant side reaction in the pyrolysis of HFAM is the recombination of the CF_3 radicals to form C_2F_6 . However C_2F_6 is a fully saturated molecule known to be unreactive towards silicon. Since the pyrolysis can be carried out almost quantitatively, this scheme offers the possibility of producing only CF_3 radicals and the inert molecules N_2 and C_2F_6 .

Figure 1 shows the C 1s photoemission spectra of a clean Si surface after exposure to un-pyrolized HFAM and after a dose of pyrolized HFAM. While the un-pyrolized HFAM shows the chemisorption of a CF_3N_2 fragment, it is entirely absent in the case of pyrolized HFAM. In addition, the un-pyrolized HFAM showed dissociative nitrogen adsorption, while there was no detectable N 1s peak after exposure to pyrolized HFAM. This indicates that the pyrolysis was indeed complete.

The effect of increasing the dose of pyrolized HFAM was to initiate the build-up of more graphitic and carbidic carbon. Examination of these spectra in conjunction with F 1s spectra showed that upon additional exposure, F atoms were removed from the CF_3 radicals and transferred directly to silicon. This results in the formation of a passivating carbon layer on top of the clean Si. It is therefore suggested that the buildup of such a passivating layer is responsible for the failure of CF_3 radicals to effectively etch Si, thereby increasing the selectivity of SiO_2 over Si in the absence of F atoms.

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Figure 1. Carbon 1s photoemission spectra collected with 350 eV photons. a) Si (111) exposed to 10L of $\text{CF}_3\text{N}_2\text{CF}_3$. b) Si (111) exposed to pyrolyzed $\text{CF}_3\text{N}_2\text{CF}_3$.

ON THE EFFECTS OF Ga IN THE FORMATION OF REACTIVE INTERFACES

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Metal adsorption studies on semiconductors at low coverages offer the possibility of identifying precursor states which evolve into interface states that determine the Schottky barrier. An interesting class of metal adsorbates are the transition metals, which are known to form deep levels in bulk semiconductors, and which also have been intimated by us as important in the formation process of Schottky barriers. Although very reactive even at room temperature, a stable configuration is not expected. Annealing the surface, on the other hand, may reduce inhomogeneities. Such effects have indeed been observed by annealing GaAs cleaved surfaces exposed to V and Pd for coverage ranges of 0.01 to 2 monolayers (ML). A drastic enhancement in the line shape of the Ga 3d core level spectrum to that of the clean surface ensues on both n and p-type GaAs. Whereas the Fermi level position on n-type GaAs decreases slightly relative to the valence band maximum (VBM) with annealing, on p-type GaAs decreases exceeding 300 meV are observed for coverages below 0.1 ML. Smaller changes are observed for larger coverages. These observations are inconsistent with a single intrinsic defect. They rather indicate the presence of acceptor and donor levels of different origin. Upon annealing the donor levels either evolve into levels lower in the band gap or they disappear as new donor states begin to dominate. A possible source for these states are reaction products of the metallization.

Elemental Ga is essentially the only biproduct observed during the metallization of GaAs with reactive metals, which include most of the metals studied thus far. Since Ga itself has been reported to form a Schottky barrier, the role of the two metals in the barrier formation process cannot be separated a priori without additional experiments. To understand the role of elemental Ga, we have reexamined the Ga/GaAs(110) interface. On n-type surfaces an initially slow, nearly logarithmic decrease in the position of the Fermi level is observed to a coverage of about 0.5 Å of Ga, after which a rapid decrease occurs which subsequently levels off to a value 0.6 eV above the VBM. The behavior on p-type is similar, with the exception that the band bending is constant at a value of 250 meV above the VBM over the range of 0.005 to 0.5 Å, before rapidly rising to a value near 0.6 eV above the VBM. The onset of the rapid changes in the Fermi level positions on both conductivity types coincides with the formation of metallic Ga islands. This unusual behavior suggests that a unique donor level ≈ 250 meV above the VBM is formed by the non-metallic Ga. We do not know however, if the Ga is atomic or in clusters consisting of a few atoms, although the data appears to support the former. The estimated Schottky barrier height for n-type GaAs of 0.60 ± 0.040 eV is in considerable disagreement with previous determinations.

The low value of the Ga donor level is consistent with the annealing experiments, provided that this treatment reduces the donor levels induced by the transition metals- a possibility since the position of the donor level for the bulk substitutional impurities lie generally near or below the VBM. However, it is generally observed that the Fermi level position during metallization on p-type GaAs far exceeds the Ga donor level, from which we conclude that Ga does not play a major role in the Schottky barrier formation process of reacting metals on GaAs. Furthermore, its low miscibility at room temperature with many metals suggests that the exchanged Ga is swept away from the interface as the metal grows, a phenomenon already observed for Ag grown on a GaAs surface with dispersed Ga atoms.

ELECTRONIC STRUCTURE OF $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$

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The electronic structure of the copper oxide-based superconductors^{1,2} is of considerable interest for understanding the mechanism of superconductivity at high T_c . The group of compounds with the highest T_c reported to date is exemplified by $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$. We are using a combination of state-of-the-art techniques such as photoemission, inverse photoemission, and near edge X-ray absorption fine structure (NEXAFS) in order to obtain the salient features of the Cu- and O- derived states.³

From the photoemission data, we observe a significant contribution from a thin carbonate overlayer (typically 5 Å) which was identified by its C 1s signal. Carbonate gives rise to a peak at -9.3 eV and contributes to the -4.7 eV peak.³ The carbonate ion is mostly associated with Ba since a high binding energy component of the Ba 4d core level increases with higher carbonate concentration. The NEXAFS data are unaffected by the presence of carbonate since secondary electrons with zero kinetic energy (i.e., long mean free path) are detected. We note that carbonate films may cause the weak links that limit the current carrying capacity of high T_c superconductors.

From our NEXAFS results at the Cu and O core edges we obtain the oxidation states of Cu and O, which have been observed to play a critical role for the occurrence of superconductivity. We find that Cu is in the 2+ oxidation state and that the 2p shell of the oxygen atoms is not filled completely. In a simplified picture, there are two ways to distribute the available electrons among Cu and O, always assuming fully-oxidized 1Y^{3+} and 2Ba^{2+} . One needs $2\text{Cu}^{2+} + 1\text{Cu}^{3+}$ per unit cell in order to have 7O^{2-} . Alternatively, having all Cu atoms in the 2+ oxidation state would require one oxygen in the 1- oxidation state. Our NEXAFS data favor the second picture. The Cu 3p edge has an energy position identical to that in CuO without additional structures. The Cu 2p edge behaves likewise (Fig. 1). The O 1s edge is characterized by a spike at threshold (arrow in Fig. 2) which indicates transitions from O1s into unoccupied O2p states.

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Figure 1. Near edge X-ray absorption spectra of the Cu 2p edge measured via the yield of secondary electrons. The Cu 2p edge is very similar to CuO, indicating Cu^{2+} .

Figure 2. Near edge X-ray absorption spectra of the O 1s edge measured via the yield of secondary electrons. The O 1s edge has a spike at threshold indicating unoccupied O 2p states.

CHEMICAL VAPOR DEPOSITION OF TUNGSTEN ON SILICON OXIDES

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The growth of metallic films on semiconductors via Low Pressure Chemical Vapor Deposition (LPCVD) has many advantages over traditional methods, such as evaporation or sputter deposition. One of the major advantages of LPCVD is that the chemical nature of the process allows for the ability to produce spatially selective deposits. In the present case, tungsten films are grown on silicon by exposure of silicon wafers to tungsten hexafluoride. This process is selective in that a tungsten film will grow on a bare Si substrate, but no growth will take place on silicon oxide.^{1,2} The growth of a W film on clean Si proceeds via Si diffusion through the growing W layer to the surface, so that Si can chemically reduce incoming WF_6 molecules.³ As no growth will occur on a thin (11 Å) thermally annealed oxide layer, it is suggested that this oxide layer forms a barrier to silicon atom diffusion.

To more fully understand the nature of the chemical selectivity and the role of a thin oxide layer in inhibiting the W growth, exposures were made on silicon surfaces that were only partially oxidized. A partial oxide layer was grown by exposure of a clean Si (111) wafer to 200L of O_2 at room temperature. The Si 2p spectrum of this sample showed only a small amount of Si^{4+} (i.e. fully formed SiO_2) and mostly partially oxidized Si atoms on the surface. Exposure of this sample to 1000L of WF_6 at room temperature resulted in a distribution of tungsten oxidation states which indicated an incomplete dissociation of the chemisorbed WF_6 molecules.

The W 4f distribution of this sample can be seen in the photoemission spectrum of Fig. 1. A small amount of metallic W is visible and a large amount of W 4f intensity shifted towards higher binding energy from the metallic W 4f. The shifted W 4f intensity was divided into two separate peaks for the numerical fitting shown in Fig. 1. One of these regions was shifted 3.3 eV from the metallic W 4f and the other was shifted 6.8 eV. It is likely that some of the species seen in the shifted W 4f levels of Fig. 1 are W atoms bound both to fluorine and oxygen, for example an WF_4O unit which is bound to Si through the O atom.

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Figure 1. Photoemission spectrum of a Si (111) wafer exposed to 200L of O_2 at room temperature followed by exposure to 1000L of WF_6 at room temperature. The solid line is the raw data and the dashed lines are a numerical fit to the data.

CHEMICAL SELECTIVITY IN PHOTON STIMULATED DESORPTION OF FLUORINE FROM SILICON

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The process of stimulated desorption of positive ions from surfaces has been used extensively as a means for understanding the localized bonding states and geometries of adsorbed species. We report here results from the study of F^+ desorption from Si (111) in which desorption occurred as a direct result of ionizing the 2p core level of the Si atom to which the fluorine was bonded. It was observed that the desorption yield vs. photon energy was dependant on the oxidation state of the bonding atom in that the desorption threshold at the 2p core level was shifted by chemical shift of the 2p level that was observed with photoemission. Because of this strong dependence of the PSD on the oxidation state of the bonding Si atom, the possibility exists for synchrotron-driven selective chemistry. By tuning the radiation to the core level binding energy of a species in a specific state, that species can be selectively desorbed from the sample.

The PSD yield vs. photon energy for these surfaces is in essence the local absorption spectrum of the bonding Si atom. Due to the different bond angles for the various types of silicon fluoride species, the ions were emitted from the sample along different directions for each of the chemically distinct species. In particular, desorption of F^+ from Si atoms in the 1^+ state was observed in the normal direction from the sample, while F^+ from the 2^+ and the 3^+ oxidation states desorbed at a more grazing angle. Because of this angular dependence to the PSD, the absorption spectra of Si atoms at different surface sites can be easily separated.

A surface containing a mixture of silicon fluorides can be prepared by exposure to 50L of XeF_2 .¹ The Si 2p photoemission spectrum of such a surface is shown in the bottom panel of fig. 1. The top panel of fig. 1 shows the absorption spectrum of this surface, obtained by monitoring the yield of 25 eV electrons, along with the PSD obtained with the sample normal facing the analyzer and with the sample rotated 65° from that position. Note that the onset for the absorption spectrum correlates with bulk photoemission, since the main absorption feature is the transition from a bulk Si 2p level to the conduction band minimum (CBM). The normally directed PSD signal, however, is shifted approximately 1 eV from the absorption onset, and correlates well with the position of the 2p level shifted due to bonding with a single F atom. This indicates that the PSD occurs as the 2p electron in the bonding Si atom becomes ionized.

Also shown in fig. 1 is the PSD obtained at a grazing exit angle. In this case, the peak near 102 eV is greatly attenuated, and a new peak begins to appear near 104 eV. This new peak is the PSD resulting from fluorine bonded in an SiF_3 group. Note that the off-normal PSD shows additional structure not present in the SiF PSD. This additional structure is assigned to transitions from the bonding SiF_3 Si 2p level to Rydberg-like 3s and 3p states that are present in the quasi-molecular SiF_3 unit.²

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Figure 1. The upper panel shows the photoabsorption spectrum and normal and off-normal PSD spectra for a Si (111) surface exposed to 50L of XeF_2 . The bottom panel shows the Si 2p photoemission spectrum, resolved into its spin-orbit components and shown with respect to the CBM in order to appropriately demonstrate the correlation between the photoemission and features in the PSD and absorption spectra.

Resolution Test of the Zoneplate Monochromator at Beamline U8

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Figure 1 gives the geometry of the zoneplate monochromator at beam line U8. The monochromator contains only one optical element, a free-standing zoneplate of 1000-2000 Å thick gold. There is no entrance slit. The exit slit is at a distance of 15700 mm from the source and wavelengths are tuned by a linear translation of the zoneplate.

Fig.1. Geometry of the monochromator.

The translation range of 1800 mm corresponds to tuning of about a factor 2 in wavelength or energy. There are positions to mount 5 different zoneplates; two are presently mounted and cover the range from $\lambda = 20 - 35$ and $\lambda = 32 - 59$ Å. The zoneplates were fabricated¹ for a resolution $E/\Delta E > 2000$; however, this resolution requires a source size below 0.1 mm.² Values around 200 are obtained with the present beam. The circles in Fig. 2 show the measured photocurrent from a graphite sample as a function of photon energy. For comparison, we show the graphite spectrum as published by Morar et al.³ convolved with a Gaussian of 1.4 eV halfwidth (full curve). The Gaussian alone is also plotted (dashed) in the Figure and represents the present resolution of the monochromator. We hope that a better resolution will be obtained with a smaller source size.

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Fig. 2. Measured photocurrent from a graphite sample (circles), Graphite spectrum from Ref. 3 convolved with a gaussian of 1.4 eV halfwidth (full curve) and gaussian used for the convolution (dashed).

Refractive Index Measurements of Amorphous Carbon Near its K Edge

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Direct measurements of the refractive index for soft x-rays from reflectivity data has been hampered by weak signals and surface contamination problems. Around the carbon K-edge contamination of the monochromator optics by carbon caused additional difficulties. The carbon contamination problem of the optics can be eliminated by using a zone plate monochromator with a free-standing zone plate as the only optical element for monochromatization. Reflectivity measurement from a multilayer instead from a single film increases the signal and replaces the external surface with a large number of better defined internal surfaces. Such measurements using multilayers have been previously reported at the Ti K edge (4.9keV)¹ and Ni L edge (850eV)². We report here the first measurements around the C k edge at 284 eV.

The position of the reflectivity maximum of a multilayer is slightly shifted from the position defined by the Bragg condition due to refraction and this shift can be used to determine the effective index of a multilayer which is defined as

$$\delta_{\text{eff}} = \beta\delta_1 + (1 - \beta)\delta_2 \quad (1)$$

where β is the fraction of the multilayer occupied by material 1 and $\delta_1 = 1 - n_1$, $\delta_2 = 1 - n_2$ are the refractive indices of the two components of the multilayer. The effective index is obtained from the wavelength λ and grazing angle Θ of the reflectivity maximum of a first order peak:

$$\delta_{\text{eff}} = \sin\Theta (\sin\Theta - \lambda/2p). \quad (2)$$

We used a 140-layer Co-C multilayer with a period $p=32.1 \text{ \AA}$ and a β value of 0.66 for the carbon layers and obtained δ_{eff} from measured reflectivity curves $R(\Theta)$ as shown in Fig. 1. The refractive index of carbon is obtained from eq. 1 using published values³ for the index δ_2 of cobalt. The results are given in Fig. 2 and are in reasonable agreement with the data of Henke et al.³. We used an adjustment in the zero of the Θ -scale to produce agreement between our measurements and Henke's data for $\lambda = 55 \text{ \AA}$.

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Fig.1. Measured reflectivity R versus grazing angle Θ for a 140 layer Co-C multilayer mirror (circles). The full curve is calculated with the parameters given. The larger width of the measured curve is due to slight deviations from strict periodicity and the limited resolution of the zone plate monochromator.

Fig.2. Refractive index of amorphous carbon near the carbon edge. Each point (open circle) is obtained from a reflectivity curve as that in Fig. 1. The full circles are from Ref. 3.

PHOTOIONIZATION OF ANTHRACENE

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The photoionization of anthracene dissolved in liquid alkane solvents was studied at the NSLS, beam line U9A. The purpose of the study being to investigate further the mechanism of photoionization in solution.

The observed thresholds in cyclohexane, 2,2-dimethylbutane and neopentane are 6.13, 6.12 and 6.10 eV, respectively. The photoconductivity spectrum (Fig. 1) of anthracene in cyclohexane showed a broad peak at 6.4 eV. Thus, cyclohexane is similar to neopentane and 2,2-dimethylbutane which also exhibit peaks in the photoconductivity at this energy attributed to the presence of Rydberg states. Previously it was thought that such states were not formed in liquids in which the electron mobility is low,¹ and cyclohexane is such a liquid.

Fig. 1. Yield of photoionization vs photon energy (in meV) for 5 mM anthracene in cyclohexane.

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Acknowledgment

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.

Fluorescence from Cyclohexane Isolated in an Argon Matrix

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Previous work in this program has produced detailed information about relaxation of electronic/vibronational energy transfer in gas, liquid, and solid saturated and unsaturated hydrocarbons.¹⁻³ By studying the behavior of fluorescence lifetimes and excitation spectra as functions of pressure, excitation wavelength, and quenching gas concentration, we have developed a simple model for the decay of excess energy in these systems. The smallest saturated hydrocarbons from which fluorescence has been observed contain five carbon atoms. In order to develop a detailed model for electronic energy transfer, data are needed about fluorescence from smaller, more easily described molecules. Therefore, methods must be used which may permit observation of fluorescence from these molecules. Isolation of hydrocarbon molecules in a cryogenic rare-gas matrix may achieve this goal for the following reasons. First, the molecular environment in a rare-gas matrix is relatively non-interacting. This permits control of hydrocarbon concentration while reducing the deactivation present in the neat liquid or solid. In fact, control of hydrocarbon concentration permits studies of monomer-monomer, and oligomer-oligomer interactions. Second, the relatively dilute concentration of hydrocarbon molecules in a rare gas matrix allows penetration of UV/VUV radiation into the bulk of the matrix; the high extinction coefficient of neat liquid or solid hydrocarbons for absorption of UV/VUV radiation causes surface or near-surface fluorescence, only. Also, the fluorescence quantum yield in saturated hydrocarbons is enhanced at low temperature. Therefore studies at cryogenic temperatures may permit observation of fluorescence hitherto too weak to be studied.

We have observed fluorescence from a few percent of cyclohexane in an Ar matrix in the range 14-30 K. The fluorescence lifetime is near 2.4 nsec, with an excitation wavelength near 155-165 nm. The lifetime is a weak function of temperature in the range studied. The form of the excitation spectrum is similar to that observed in the neat solid or liquid near room temperature, but is wider, so that some fluorescence may be observed with excitation whose wavelength is as short as 145 nm.

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Acknowledgement

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 of Laser-Excited Atoms

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In the past several years, we have undertaken a program of determining ground and excited state atomic photoionization cross sections using laser and synchrotron radiation.^{1,2} Measurement of photoionization cross sections over reasonably wide wavelength ranges requires the tunability of synchrotron radiation. Generation of large concentrations of excited-state atoms requires an intense source of pumping radiation within a narrow bandwidth, such as that available from an etalon-equipped argon-ion pumped dye laser. The use of laser and synchrotron sources, together, therefore, in a synergistic manner, exploits the benefits of both devices.

We have measured photoionization cross sections of ground state Mg atoms, and excited state Na(3p) atoms.² The next logical step in the measurement of the photoionization cross section of an excited atom such as Ba(6p). The photoionization spectrum of this species will exhibit resonances from two-electron autoionizing states embedded in the continuum, following excitation of ground state Ba by green light. Last year, detection of ground and excited state Ba photoionization was demonstrated, but only weakly. Evidence was also obtained for Ba ionization from "energy pooling", collisional ladder-climbing processes. This year's experiments were performed using a modified apparatus, which eliminated mass selection, and a better detector. Photoion signals were obtained from ground state Ba, and evidence was obtained for at least six autoionizing resonances, in the ground state spectrum. Excited state signals were still too weak for reliable observation. The most important reason for the weak Ba(6p) signal appears to be the relatively low photon flux from beam line U9A. Another attempt will be made to measure the Ba(6p) photoionization cross section, using the greater flux available from beam line U11.

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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.

TIME-RESOLVED FLUORESCENCE STUDY OF VUV LIGHT INDUCED REACTIONS OF CHLORINE OR CYANOGEN CONTAINING MOLECULES/RARE-GAS MIXTURES

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During FY 1987, a one-week (June 1 - June 5) experiment on gas-phase vuv photochemistry was conducted at the U9B beamline. This work was done in collaboration with Jack Preses and Ralph Weston of the Chemistry Department at BNL. The main thrust of the experiment was to investigate the reaction dynamics of vuv light activated reactive mixtures. Specifically, fluorescence excitation spectra and some time-resolved fluorescence measurements on mixtures of Xe or Kr with Cl_2 , HCl , CCl_4 , COCl_2 , COClF , and C_2N_2 were made.

Interest in high power excimer lasers in recent years has prompted several studies of light induced reactions between rare gas atoms and halogen containing molecules.¹ Much of this work was aimed at understanding the kinetic processes that are relevant to excimer laser systems, namely, reactive mixtures of Cl_2 and HCl with Ar, Kr, and Xe.² In this work, we intend to examine the chemical dynamics of highly excited polyatomics colliding with inert gases such as Xe and Kr. Particular emphasis is directed at investigating the importance of electronic state-specificity in the molecular precursor and its relation to pertinent issues such as the branching ratio, quantum efficiency, and internal energy contents of the resultant excited products. This would provide new insight to the reaction mechanism for producing excited excimers and answer questions such as whether differences exist in transitions involving valence, Rydberg, or ion-pair states, and perhaps provide useful information related to the photodissociation dynamics of the parent species. Furthermore, it is intended that the vuv excitation technique be used as a selective means for producing new excimers, allowing their identification and characterization.

In the first set of experiments, it was determined that excimer emission was detected only when the vuv light excitation involves relatively long lived (on the orders of ns) upper electronic states of the mixture species. This was illustrated in the fluorescence excitation spectrum of Kr/Cl_2 in the 110 to 145 nm region obtained by monitoring KrCl C-X emission. The spectrum mimics the fluorescence excitation spectrum of Cl_2 emission. Since in the case of Cl_2 , the reduction in fluorescence quantum efficiency in these states is believed to be due primarily to predissociation. The quantum yield of the KrCl^* is, therefore, a mere reflection of the efficiency of how the reaction rate at the operating pressure competes with the fluorescence lifetime of the states. This is also indicative that weak XeCl emission was detected when HCl/Xe mixtures were excited in the spectral region where HCl is highly predissociative. A high spectral resolution experiment which can resolve rotational structures will be of particular value to further verify this conclusion. Unfortunately, the needed spectral resolution is unattainable with the current apparatus. In experiments that involved mixtures of Kr or Xe with Cl containing polyatomics (CCl_4 , COCl_2 , and COClF), preliminary results indicate higher fluorescence quantum efficiencies were obtained based on their absorption cross sections and estimated lifetimes. It appears that there is also a distinct drop off in fluorescence intensity going from Xe to Kr mixtures, which is not observed in the similar mixtures involving Cl_2 with comparable amount of photoexcitation. This may simply be due to a significant difference in the energetics for breaking a Cl-Cl and C-Cl bond, and for forming an excited excimer complex. This suggests that either different reactive pathways or species (or same species, but different energy levels) are at work. One possibility could be that, in the excitation of COCl_2 mixtures, for example, Cl_2 in a lower electronic state than can be generated by directly excited Cl_2 is produced in the photolysis. Excited chlorine molecules in this lower electronic state can have a much longer lifetime than its parent precursor and therefore can react more effectively. Because of the lower excitation in the reactive species, it can generate only the lower energy products (XeCl^* , but not KrCl^*). More detailed experimental measurements are necessary before this question can be resolved. One interesting observation was also made in the photoexcitation of Kr or Xe/ C_2N_2 mixtures. Emission in the near uv and visible was detected when electronic resonances of Xe and C_2N_2 (but not Kr) were excited. Since only bandpass filters were used to sort out the emission bands, we were not able to unambiguously identify the emitting species. It is possible a lot of the emission is due to B and A states of CN radicals. The emission observed when Xe is excited can be attributed to a photosensitizing process where the excited atom transferred its energy to the C_2N_2 molecules and resulted in excited CN photofragments. However, the negative Kr result seems to rule out that emission was primarily from excited CN radicals, since in that case comparable emission would be expected for Kr excitation. It is conceivable that emission is indeed coming from an excited Xe-CN complex. Additional measurements, emission spectra in particular, will be conducted to determine this observation.

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NOTE: This work is sponsored by the Los Alamos National Laboratory

CIRCULAR DICHROISM OF SYNTHETIC RNAs IN THE VACUUM ULTRAVIOLET

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Double-stranded DNAs in the A conformation generally have large positive circular dichroism (CD) bands at or about 185nm, the magnitudes of which increase with G·C content.¹ We were interested in (a) whether large VUV CD spectral bands also generally appear upon base pairing of double-stranded RNAs and (b), if so, whether these bands depend simply on base composition or also depend on the sequence. Therefore, we measured the VUV CD of double- and single-stranded synthetic RNAs containing different nearest neighbors. The CD spectra of two additional single strands were estimated, using the nearest-neighbor approximation, from the measured spectra of oligomers. The RNAs measured were: poly[r(A-U)·r(A-U)], heat-denatured poly[r(A-U)], poly[r(A)·r(U)], poly[r(A)], poly[r(U)], poly[r(G)·r(C)], poly[r(C)], GpG, GpC, and CpG. The spectra of poly[r(G-C)·r(G-C)], CMP, and GMP were generously communicated by J. Riazance and W. C. Johnson Jr. (OR State U.).

The VUV CD spectra of the double-stranded RNAs did have large positive bands. The main positive VUV band was centered at 185nm for (G·C)-containing RNAs and at 177nm for (A·U)-containing RNAs. Figure 1 shows difference spectra obtained by subtracting spectra of the component single strands from the spectra of the double strands. Such difference spectra show the CD changes induced by base pairing. For both the (G·C)-containing and (A·U)-containing polymers, the main positive VUV CD bands were also present in the difference spectra and thus were due to base pairing. The similarities in the 174-220nm region between the difference spectra of the two (A·U)-containing polymers, and the similarities between the difference spectra of the two (G·C)-containing polymers, indicated that nearest neighbors had little effect on the VUV bands induced by base pairing. These similarities were in marked contrast to differences in the longer wavelength region, where nearest-neighbor contributions dominate. Since A·U and G·C base pairs each make distinct contributions to the CD in the 174-220nm region, it may be possible to use this region of the spectrum to estimate the amount of A·U and G·C base pairs in a natural RNA.

Fig. 1 CD spectra of double-stranded RNAs minus the CD spectra of the corresponding single-stranded RNAs. (···) poly[r(G-C)·r(G-C)]; (---) poly[r(G)·r(C)]; (—) poly[r(A-U)·r(A-U)]; (-·-) poly[r(A)·r(U)]

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This work was supported by NIH Research Grant GM 19060, by Grant AT-503 from the Robert A. Welch Foundation, and by the NSLS Faculty-Student Support Program.

FLUORESCENCE DECAY PROFILES OF COVALENT ENNZO(A)PYRENE DIOL EPOXIDE ENANTIOMER - DNA ADDUCTS*

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This investigation is a part of an ongoing study of the covalent adducts of the carcinogen benzo(a)pyrene diol epoxide (BaPDE) and DNA and their physical conformations [1]. In the past we have studied the adduct configurations resulting from the addition of a racemic mixture of BaPDE to calf thymus DNA. The fluorescence decay profiles of these adducts are multiexponential, indicating heterogeneity of binding sites. In order to better understand this heterogeneity we have this time focused on the adducts of the pure (+) and (-) enantiomers of the hydrocarbon. The study of the enantiomers is further interesting due to their radically different biological activities ((+)>>(-)). The narrow, high repetition, high intensity pulse of the National Synchrotron Light Source was an ideal excitation source in these measurements due to the rapid decay of the shortest lifetime components of the adducts, and due to the low concentrations of fluorophores in these samples (and consequently inherent low signal intensities).

Data with emission at 400 nm was collected at two different excitation wavelengths: 346 nm, the absorption maximum of (+) BaPDE-DNA, and 352 nm, the absorption maximum for (-) BaPDE-DNA; it should be noted however, that the adducts of each enantiomer exhibit some absorption at or around both wavelengths, (-) BaPDE-DNA being the more heterogeneous of the two. This data is summarized in Table 1. A broad excimer emission band with a 472 nm maximum, but overlapping the 400 nm band, was found to contain 1.8 and 13 ns decay components.

Table 1. Fluorescence Lifetimes in Nanoseconds

	Excitation Wavelengths (emission of 400 nm)			
	346 nm		352 nm	
(+) BaPDE-DNA	$a_1 = 0.45$	$\tau_1 = 1.4$	$a_1 = 0.44$	$\tau_1 = 0.8$
	$a_2 = 0.37$	$\tau_2 = 5.0$	$a_2 = 0.41$	$\tau_2 = 2.7$
	$a_3 = 0.13$	$\tau_3 = 19$	$a_3 = 0.14$	$\tau_3 = 15$
	$a_4 = 0.05$	$\tau_4 = 130^a$		
(-) BaPDE-DNA	$a_1 = 0.69$	$\tau_1 = 0.8$	$a_1 = 0.37$	$\tau_1 = 0.8$
	$a_2 = 0.19$	$\tau_2 = 3.1$	$a_2 = 0.44$	$\tau_2 = 3.1$
	$a_3 = 0.11$	$\tau_3 = 22$	$a_3 = 0.19$	$\tau_3 = 15$
	$a_4 = 0.05$	$\tau_4 = 130^a$		

*The 130 ns lifetime component was determined independently, using a conventional flash lamp as a light source. This component was then held fixed in the analysis of the synchrotron data. It is attributed to dissociated adducts in the form of BaP tetraols which have an absorption maximum at 343 nm and almost no absorption at 352 nm; thus no a_4 was fixed at 352 nm.

The major difference between data for (+) and (-) BaPDE-DNA lies in the overall slower decay of the (+) BaPDE-DNA fluorescence in comparison to that of the (-) adducts. In addition, τ_2 (which is longer than τ_1) is more prevalent in the (+) adduct than in the (-) adduct solutions. The minor τ_3 components are attributed to the broad emission excimer fluorescence.

Since the $\tau_1:\tau_2$ ratios (τ_1 and τ_2 are the decay components attributed to covalent adducts) are not in accordance with the distribution of binding site types as known from absorption, linear dichroism [2] and HPLC [3] measurements ((+) BaPDE-DNA, for example, appears to be about 94% homogeneous), it seems probable that the $\tau_1:\tau_2$ ratios are related in part to the base sequences of the DNA. To address this, we have begun fluorescence decay measurements using adducts of (+) and (-) BaPDE with selected synthetic polynucleotides of known sequence.

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* This work was supported by U.S. DOE contract DE-AC02-78EV04959, and by the O.H.E.R., U.S.D.O.E.

ARGON MATRIX ISOLATION FLUOROMETER*

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A matrix isolation fluorometer was designed and built at beamline U9B, with the capability of sublimating solids into an inert gas matrix at cryogenic temperatures. This fluorometer will be utilized for the spectroscopic and time dependent study of nucleic acid bases in an argon matrix.

The excitation wavelength is selected by a vacuum monochromator. The emission is passed through an air monochromator on to a cooled photon counting side window photomultiplier tube. The sample holder is attached to a helium expansion cryotip, and is placed in a vacuum chamber. The solid state nucleic acids are placed in a tantalum boat in the same vacuum chamber, held by two copper electrodes, with an opening toward the sample holder. To form a matrix, the tantalum boat is heated by slowly increasing the current passed through it, the nucleic acids are sublimated and deposited on the 13°K quartz or magnesium fluoride window on the sample holder. Argon is simultaneously introduced through thin copper tubing bent so that its opening is just above the tantalum boat opening and pointed toward the window. The flow of argon gas is controlled by an adjustable leak valve.

Detection of the absorption properties of a deposited matrix is made possible by a hole in the sample holder along the excitation light path.

The sample holder can be turned in different directions depending on whether a matrix is being deposited, an absorption spectrum recorded, or fluorescence properties investigated.

To date, an adenine-argon matrix has been successfully deposited, in a manner which proved to be reproducible. The absorption spectrum of this matrix is shown in fig. 1; it corresponds to spectra of adenine in solutions.¹

Fig. 1. Absorption spectrum of an adenine-argon matrix.

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* This work was supported by the O.H.E.R. of the U.S. Department Of Energy.

Electronic Structure of the Icosahedral and Other Phases of Aluminum - Manganese Alloys Studied by Soft X-Ray Emission Spectroscopy

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Intermetallic phases have been discovered¹ which exhibit icosahedral or decagonal (T phase) symmetries that are impossible for ordinary crystalline material. There have been many interpretations of the structure of this material. One would like to determine where the atoms are with respect to sites in the unit cell, the tiles, or the structural element. This important quantity has not been definitively established. Furthermore the nonperiodic structure of these materials makes the calculation of the band structure a challenge. Several authors²⁻⁴ have modeled the electronic properties of these materials, but there has been almost no measurement of their band structure. Soft x-ray emission (SXE) yields valence band emission spectra proportional to the partial density of states (PDOS) localized at the emitting atom. We report the first measurement of the SXE spectra of the $L_{2,3}$ emission bands in the icosahedral and decagonal (T phase) and the related α cubic phase of Al-Mn-Si.

The measurements were made from a melt spun ribbon prepared at the NBS. Our ultra sensitive soft x-ray spectrometer⁵ installed on U-10 was used to obtain the spectra, which were excited by an electron beam. The results are summarized in Figure 1. Fig. 1a) is an enlargement of the spectral range near the photon energy corresponding to transitions of the electrons near the Fermi energy ϵ_F to 2p core holes. Fig. 1b) shows a comparison of the PDOS between 62 and 67 eV, corresponding to small values of the k vector.

Figure 1:

$L_{2,3}$ spectra of aluminum.

- a) Shows the spectra on an expanded scale near ϵ_F .
- b) Shows the spectra on an expanded scale for lower photon energies. Al, T, α , and I identify the curves for pure aluminum, the T phase, the α cubic phase and the icosahedral phase of the materials, respectively.

In summary, we find the spectra of different alloy phases very similar. This observation suggests that the quasicrystalline phase produces a small perturbation of the electronic density of states. We observe a chemical shift of 0.2 eV between the alloys and pure aluminum, which is consistent with the shift one would observe by accounting for the redistribution of the electrons localized at the aluminum and the change in the volume available to the electrons at the aluminum sites. We observe a chemical shift of less than 0.1 eV between alloys of the crystalline phase and the quasicrystalline phase, which contradicts one model² that predicted a 0.9 eV shift. We also observe a diminution in the partial DOS near ϵ_F of the quasicrystalline alloy compared to the crystalline alloy. Two theoretical models^{2,3} predict an enhancement of the DOS near ϵ_F which was not observed. These results provide new information to guide the calculations of the electronic band structure of these materials.

Acknowledgements:

The authors are grateful to Mr. F. Biancaneello of the Metallurgy Division at the National Bureau of Standards for providing the alloy samples used in this research. This research is supported by NSF grant DMR-8593541 (UT), by the Science Alliance grant from the state of Tennessee (UT), by USDOE contract DE-AC05-84OR21400 (ORNL), and by the U. S. Air Force Office of Scientific Research under contract ISSA87-0050 (NBS). The research was carried out in part at the National Synchrotron Light Source at Brookhaven National Laboratory, supported by USDOE contract DE-AC02-76CH00016.

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SOFT X-RAY EMISSION STUDIES OF $\text{Al}_x\text{Ga}_{1-x}\text{As}$ COMPOUNDS

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The alloy semiconductor compounds, $\text{Al}_x\text{Ga}_{1-x}\text{As}$, have been extensively studied because of their importance in semiconductor technology. Most of the experimental data of these compounds are obtained by either optical measurement or photoemission spectroscopy, and the partial density of states have not been studied. The $\text{Al } L_{2,3}$ emission spectra in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ compounds have been systematically measured for the first time.

Figure 1 shows $\text{Al } L_{2,3}$ emission spectra for $x=0.05, 0.1, 0.2, 0.3, 0.4, 0.6$, and 0.8 alloys with all spectra normalized to the P2 peak height. The qualitative changes we observe with increasing Al concentration are the following: (1) No changes occur in peak P3 in either position or magnitude; (2) Peak P2 narrows and increase in amplitude so that its area is nearly unchanged; and (3) The high energy shoulder is unchanged except that the position of the valence band maximum (VBM) decreases with increasing Al content.

There is almost no shift between peaks P2 and P3 in SXE spectra, while there are more than 0.3 eV changed in PE data obtained by Ludeke et al. The observed change in the position of the VBM is plotted in Figure 2. A total shift of 0.75 eV is observed that may be fitted by two straight line curves that intersect at about $x=0.38$ near the concentration of the fundamental bandgap transition. The inclusion of the cation d-orbitals as suggested by Wei et al. may partially explain the suppression of the top of the valence band. The observed nonlinear change in the VBM is probably a hybridization effect similar to fundamental bandgap observed in optical data.

Figure 1. SXE $L_{2,3}$ spectra of Al in $\text{Al}_x\text{Ga}_{1-x}\text{As}$

Figure 2. Energy position of valence band maximum.

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The research was supported by NSF grant DMR-8503541, by the Science Alliance grant from the state of Tennessee, and by the US DOE under contract DE-AC05-84OR21400 with Martin Marietta Energy System. The research was carried in part at the National Synchrotron Light Source, which is supported by the US Department of Energy under contract DE-AC02-76CH00016.

Soft X-ray Absorption and Emission Spectra and the Electronic Structure of the $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ Superconductor

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We present measurements of soft x-ray emission and total photoelectron yield of $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$. Our total photoelectron yield measurements near the 3p ionization threshold in Cu support the contention that Cu is in the +2 valence state.^{1,2} We have used electron-beam excited soft x-ray emission spectra to measure the p-type partial density of states (p-PDOS) localized on O, Ba, and Y sites. For the elements (Y, Ba, and O) the major peak in the soft x-ray emission spectra lies about 3.4 to 4.0 eV below ϵ_F rather than at the ~ 2 eV that would be expected from p-PDOS derived from ground state band structure calculations.^{3,4} We have also observed the $L_{2,3}$ emission spectrum of Cu in $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$, which maps out valence states of d symmetry. The maximum in the PDOS lies about 2.5 eV below ϵ_F . These observations place the d and p bands about 2 eV and 4 eV below ϵ_F respectively. This evidence is supported more strongly by a tight binding calculation⁴ of the band structure and the DOS than by a highly precise local density band study³ where the O p states have a large DOS at 2 eV. BE and are embedded in the copper d bands which have the largest DOS at about 4 eV. The present measurements have been made both at room temperature and at 85 K. No difference in the p-PDOS was observed at the two temperatures. This is consistent with observations that $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ does not undergo a structural phase change between T_c and room temperature.

Figure 1:

a) Total quantum yield for superconducting $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ as a function of the photon energy. A defines the energy region corresponding to that required for the promotion of a 3p core electron in Cu to the conduction band. The energy band denoted by B is the absorption by 4d core electrons in Ba.

b) Intensity of soft x-ray fluorescence excited by 2 keV electrons vs. photon energy. C denotes the energy position of the $\text{N}_{2,3}\text{M}_{4,5}$ transition in Y in second order reflection from the grating; F is the first order signal of this transition. D is the energy region corresponding to Ba inner shell transitions $\text{O}_{2,3}\text{N}_{4,5}$ and transitions between the valence electrons and the Ba 4d hole states.

Acknowledgements:

The authors are grateful to Dr. L. Bennett of the Alloy Physics Division at the National Bureau of Standards for verifying the superconducting nature of the samples. We also appreciate the hospitality shown us at the Hamburg Synchrotron radiation source, and we are grateful to C. Kunz for the use of his monochromator. Assistance from the operating staff of the NBS-SURF II synchrotron light source is gratefully acknowledged. This research is supported by NSF grant DMR-8593541 (UT), by the Science Alliance grant from the state of Tennessee (UT), by USDOE contract DE-AC05-84OR21400 (ORNL), and by the U. S. Air Force Office of Scientific Research under contract ISSA87-0050 (NBS). The research was carried out in part at the National Synchrotron Light Source at Brookhaven National Laboratory, supported by USDOE contract DE-AC02-76CH00016.

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THE $Al_{2,3}$ AND Mg DOUBLE IONIZATION EMISSION SPECTRA OF DILUTE Al IN Mg ALLOYS

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The $Al_{2,3}$ spectra for dilute alloys of Al (0.5, 1.0, 2.0 at. %) in Mg , and the Mg L satellite spectra produced in atoms with doubly ionized $2p$ core levels has been measured. Two spectra can be viewed as isolated impurity atoms with a single excess charge in final state imbedded in a Mg host lattice, and expected to have similar features according to the equivalent core approximation (ECA)¹. Under same assumption, the Auger KL_1V spectrum of Mg with an excess core hole in the final state of the transition should give some information similar to SXE spectra, although s and p states with approximately equal probability in radiative transition.

The spectra of the Mg satellite and Al $L_{2,3}$ for Al in Mg alloys and pure Mg are shown in Figure 1. We report for the first time observation of the L_3-L_1 intercore transition for the satellite spectrum at 54.4 ± 0.1 eV. The weaker high energy structure from about 67 to 74 eV in pure Mg satellite we observe may result from the radiative decay of the previously unobserved $1S_0$ state.

In Figure 2, the spectra of the Al impurity, Mg satellite, and Mg KL_1V from Lasser et al.² are compared. Each is observed to have a prominent low energy peak associated with the screening charge, but the central peak in the Mg satellite spectrum, which corresponds to a band structure feature in pure Mg has no counterpart in the Al impurity spectrum. A possible reason for the dissimilarity between Al impurity and Mg satellite spectra is the s -like valence orbitals penetrate inside the core level sphere, and thus see different potentials for the Al impurity and for Mg atoms with an extra $2p$ core hole. Clearly, a more sophisticated approach than the ECA is required for the interpretation of SXE and other core level spectra.

Fig. 1 The Mg L -satellite and Al $L_{2,3}$ spectra for Mg metal and Al in Mg alloys. The spectra are labeled with the Al content in atomic percent.

Fig. 2 The Mg L satellite, the 1 at % Al $L_{2,3}$, and the KL_1V Auger spectra compared. (...) Al impurity, (---) KL_1V Auger, (—) Mg satellite. The Auger spectrum was taken from Ref. 5.

Supported in part by NSF grant DMR-8503541, DOE under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, and the Science Alliance Center of Excellence grant from the state of Tennessee. The beamline U-10A at Brookhaven National Laboratory is supported by DOE DE-AC02-76CH00016.

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PHOTODESORPTION FROM LHe TEMPERATURE BEAM TUBE SURFACES

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Photodesorption from pure (4N) aluminum and stainless steel, both at LHe temperature, has been investigated. Photodesorption from pure aluminum was found to be approximately equal to photodesorption from stainless steel and copper which had been measured previously. The present measurements on stainless steel were made up to integrated photon doses four times that of the previous measurements. These measurements confirmed hints from the earlier data that the H_2 pressure within the experimental beam tube rises with increasing photon dose. This is shown in Fig. 1. This rise is thought to be associated with the condensation of desorbed H_2 on the inner surface of the cold beam tube. Figure 1 also shows successive cool-downs of the beam tube. The beam tube was warmed above the condensation temperature of H_2 between the cool-downs and the H_2 pumped away. After a warm-up and recool-down the H_2 pressure rise due to photodesorption decreased to approximately the initial level. It then began to increase again, achieving pressures at high dose slightly below the first cool-down pressures. This behavior is suggestive of the clean up process that is observed in electron storage rings, although this clean up requires warming the beam tube. During each warm-up, a measurement was made of the amount of H_2 gas desorbed during the previous cool-down and exposure. This amount of H_2 gas was significantly less than that expected from room temperature photodesorption measurements. This hint of a temperature effect for photodesorption will be followed up in future experiments.

Fig. 1. Hydrogen pressure rise at the detector vs. photon dose.

* Operated by the Universities Research Association for the Department of Energy.

PHOTOIONIZATION STUDIES OF A SELF-REACTIVE VAN DER WAALS COMPLEX: 1,3-BUTADIENE-SULFUR DIOXIDE

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The existence of weak complexes of reactants prior to their transformation to products has long been studied in condensed phases, where such complexes often profoundly influence reaction pathways, yields and rates. It is to be anticipated that the additional detail obtainable in molecular beam studies will advance the understanding of these reactions. One such complex is 1,3-butadiene·SO₂, which undergoes an addition reaction to produce sulfolene, $\text{C}_4\text{H}_6\text{SO}_2$, but does so slowly enough that its photoionization, as well as that of its reaction product, can be studied. Efficiency functions were measured using a photoionization mass spectrometer in which a molecular beam of target complexes, formed by a skimmed and recollimated free jet expansion of 1:4 1,3-butadiene + SO₂, was made to intersect the tunable VUV beam from the monochromator on U-11. The detector is a channeltron operated in the ion-counting mode. Careful analysis established the relative densities of dimers and trimers in the molecular beam, at nozzle pressures small enough that larger clusters are unimportant. The dissociation energy at 0 K of 1,3-C₄H₆·SO₂ was measured by the spectrum-stripping method (1984 NSLS Annual Report) to be $3.24 \pm 0.48 \text{ kcal mol}^{-1}$, while the energy needed for the process $(1,3\text{-C}_4\text{H}_6\text{·SO}_2)^+ \rightarrow \text{C}_4\text{H}_6^+ + \text{SO}_2$ was found to be $3.27 \pm 0.86 \text{ kcal mol}^{-1}$, much smaller than expected. Comparisons of photoion efficiency functions and ion yield spectra established that 1,3-butadiene·SO₂ and sulfolene are different species. Sulfolene's ionization potential was measured to be $9.80 \pm 0.05 \text{ eV}$, and the C₄H₆⁺ appearance potential $10.10 \pm 0.03 \text{ eV}$. Thus, the sulfolene ion is already unstable above 0.3 eV of excitation, and this is reflected in its very small yield. Also, from Fig. 1 we see that the sulfolene ion is more stable than $(1,3\text{-C}_4\text{H}_6\text{·SO}_2)^+$, but only by 4 kcal mol⁻¹. We found that the reaction 1,3-butadiene + SO₂ → sulfolene is exothermic by 1.03 eV (24 kcal mol⁻¹), consistent with the literature value of $23 \pm 2 \text{ kcal mol}^{-1}$ from bulk rate experiments. The rearrangement process $1,3\text{-C}_4\text{H}_6\text{·SO}_2 + h\nu \rightarrow \text{C}_4\text{H}_6\text{SO}^+ + \text{O}$ was discovered; it occurs in very low yield. The observation of C₄H₆SO⁺ reported earlier was shown to stem from the dissociative photoionization of trimers, the yield from which is much larger. Also, the efficiency functions for the two processes differ markedly. The close similarity in dissociation energy and in the efficiency function for producing C₄H₆⁺, to the corresponding properties for trans-2-butene·SO₂ leads us to speculate that the SO₂ molecule associates with only one of the two double bonds in butadiene, the ground state of which is transoid. The cisoid structure, more energetic by 2.5 kcal mol⁻¹, must be achieved for addition to form sulfolene to occur.

Fig. 1. Energy diagram for the system 1,3-butadiene + SO₂. Transition energies are given in electron volts. Values measured in this work are underlined. Refinement of these numbers is still in progress.

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.

Dissociative Rearrangement in the Photoionization of Weak Molecular Complexes

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The special dissociative photoionization process in van der Waals dimers and trimers in which atoms transfer from one moiety to another is being studied, and has revealed itself to be a rich and general new area for the investigation of chemical dynamics. In addition, this process provides an extremely promising way to prepare and study species that were previously unknown, or that are especially interesting but difficult to make by other techniques. The target complexes are prepared in molecular beams by recollimation of skimmed free-jet expansions of gas mixtures, and made to undergo single-photon interactions with the tunable VUV beams from the monochromator of line U-11. To measure photoefficiency functions a quadrupole mass spectrometer is used to select the photoions of interest, and detection is by means of a channeltron operated in the ion-counting mode. Studies to date have focused on the species $C_6H_6Cl^+$ from complexes of C_6H_6 and HCl , $C_2H_4Cl^+$ from C_2H_4 and HCl , $C_4H_6SO^+$ from 1,3-butadiene and SO_2 , $C_6H_5^+$ and HBr_2^+ from allyl bromide and argon, and $HClBr^+$ from allyl bromide and HCl . The products from the heteroclusters, e.g. $C_6H_6Cl^+$, $C_2H_4Cl^+$, $C_4H_6SO^+$, all display onsets that are markedly higher in energy than their true thresholds (e.g. from 0.7 eV above for $C_2H_4Cl^+$ to 3.0 eV above for $C_6H_6Cl^+$). In addition, in each case the yield from heterotrimers vastly exceeds that from heterodimers, as illustrated in Fig. 1 for the production of $C_2H_4Cl^+$. Indeed, sometimes no yield from dimers can be detected at all, as is the case with $C_6H_6Cl^+$ from $C_6H_6 \cdot HCl$. The photoionization efficiency function for production from dimers can display pronounced structure, as is detailed in Fig. 2 for the production of $C_2H_4Cl^+$ from $C_2H_4 \cdot HCl$. These results show that the products from heteroclusters are born with substantial excitation energies, which makes their efficient survival dependent on the presence of a third "solvent" molecule whose excitation and ejection from the cluster serves as the necessary energy sink, hence the greatly enhanced yields from trimers relative to dimers. Also, since there are always low-energy dissociative pathways available via the characteristic weak bonds of the complexes, these species can only be produced in highly nonstatistical processes. For the survivors of the production from dimers, one therefore expects the number of available pathways to be quite small, very likely only one, and this would allow the appearance of prominent structure, as exemplified by the peak at 15 eV in Fig. 2.

Fig. 1. Closed circles: yield of $C_2H_4Cl^+$ from the dissociative photoionization of trimers, i.e. $(C_2H_4)_2HCl$ plus $C_2H_4(HCl)_2$. Open squares: yield, on the same scale, of $C_2H_4Cl^+$ from the weak complex $C_2H_4 \cdot HCl$. Abscissa gives photon energy.

Fig. 2. Yield of $C_2H_4Cl^+$ from the dissociative photoionization of the weak complex $C_2H_4 \cdot HCl$, as a function of photon energy.

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.

AUGER PHOTOELECTRON COINCIDENCE SPECTROSCOPY OF Al(100)+O

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Auger Photoelectron Coincidence Spectroscopy (APECS) using a laboratory x-ray source was developed by Haak et al¹. We have extended this technique to include the brightness and tunability of synchrotron radiation. In the APECS technique two electron energy analyzers are used. One is tuned to the energy of a photoelectron, and the other to an auger energy associated with the decay of the photohole. A coincidence is recorded if and only if an electron arrives in each analyzer simultaneously. One analyzer is swept in energy, and the other is kept fixed. Both coincidence and singles (ordinary photoemission) spectra are recorded simultaneously for comparison.

The purpose of this technique is the enhancement of ordinary photoemission techniques. The advantages are the following: All uncorrelated background is removed; Overlapping spectra from alloys can be separated; Complex many body structure (magnetic effects, multiplet and shakeup structure) can be untangled; The coincidence technique has about twice the surface sensitivity of ordinary photoemission.

The first two points are illustrated in the data below from Al(100) covered with 30 L oxygen. The top panel shows a full singles scan at a photon energy of 120 eV. The oxygen 2p level is at 108 eV, the aluminum and aluminum oxide LVV auger spectra overlap and stretch from 40 to 70 eV, the aluminum 2p level is at 42 eV (arrow 2) and the aluminum oxide (aluminum 2p, arrow 1) is at 40 eV. The second panel compares a singles sweep through the core level region to the coincidence spectrum, with the fixed analyzer at 68 eV (arrow 3), the high energy part of the auger spectrum. In the coincidence spectrum the oxide core is completely removed, indicating that the oxide core does not decay via 68 eV auger electrons. In addition, the background under the singles spectrum is removed. The bottom two panels show sweeps through the auger region, and illustrate how the complex overlapping aluminum and aluminum oxide spectra are completely separable by moving the fixed analyzer from the oxide core (3rd panel) to the metal core (bottom panel). The removal of uncorrelated background is again seen.

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Al(100) + 30L O₂
Auger - Photoelectron coincidence
First data August 1987

Angle-Resolved Photoemission Determination of the NiAl Band Structure and Fermi Surface

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We have carried out an extensive study of the experimental band structure of NiAl using the (100) face of this crystal. The crystal surface was cleaned in situ by Ne sputtering and subsequently annealed to 950–1000°C, which produced a well ordered surface that exhibited a (1×1) LEED pattern. NiAl has a CsCl-type structure which has two atoms per unit cell. In k -space, the Brillouin zone is a simple cubic shown in Figure 1a. The simplicity of the cubic Brillouin zone makes it possible to measure the Fermi surface by photoemission. The crystal was oriented such that $\text{Al}\|\bar{\chi}$. Using s-polarized light and moving the analyzer to the zone boundary (χ of the surface Brillouin zone), the transition of the Δ_1 band (seventh band) was found to be very strong at 16 eV photon energy (this photon energy was found to connect the initial state at χ_1 to final state χ_2 or χ_3). Moving the analyzer collection angle back toward $\bar{\Gamma}$, the Fermi level crossing the Δ_1 band was observed at $k_{\parallel} = 0.74 \pm 0.02 \text{ \AA}$. This determined point A in the Fermi surface cross section shown in Figure 1b. Due to the high symmetry of the cubic Brillouin zone, we only need to determine the Fermi surface in 1/8 of the zone and the entire Fermi surface can be generated by symmetry operation. Starting from point A in Figure 1b, we determine the Fermi surface by changing k_{perp} , i.e., by increasing photon energy from 16 eV and by changing the analyzer collection angle slightly such that we can follow the Fermi level crossing at a different $k_{\parallel}$ as photon energy is increased. Point B in Figure 1b was found at $h\nu = 25 \text{ eV}$. The k_{perp} at this point is obtained by the following simple relationship assuming a free electron final band

$$h\nu - E_i = (\hbar^2/2m) k_{\parallel}^2 + (\hbar^2/2m)(k_{\text{perp}} + G)^2 - V_0$$

Since $E_i = 0$ at the Fermi level, k_{perp} was found to be $0.80 \pm 0.02 \text{ \AA}$ which is equal to $k_{\parallel}$ at point B. The Fermi surface obtained in this experiment is found to be in agreement with those obtained graphically from the energy band plot of D.J. Nagel¹ using a self-consistent APW calculation with a Slater X α exchange.

The high symmetry points in the NiAl band structure were determined by measuring both normal and off-normal emission. Figure 2 plots the variation between the experimentally determined critical points (E_m) and the self-consistent APW calculation by Nagel¹ (E_c). The dotted line is the data from Ni (scaled down to half the values) taken from reference 2 where the comparison was made with calculation by Wang and Callaway. Figure 2 shows that the discrepancy with theory follows the same trend for both Ni and NiAl. If we treat Figure 2 as the self-energy correction, then it clearly indicates that the d hole is more localized in Ni than in NiAl. Upon alloying with Al, hybridization with Al s,p electrons make the Ni d electron orbitals in NiAl more delocalized as compared to Ni d orbitals in its elemental form. As a consequence, we could expect a larger self-energy correction for Ni due to d-hole localization. A more detailed discussion on the comparison to theory will be followed in our future publication.

Acknowledgements

The synchrotron beam line was funded and supported by NSF/MRL program DMR-8519059, and by the Division of Materials Science, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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Fig. 1.

Fig. 2. E_c (eV)

PHOTOELECTRON DIFFRACTION FROM LANGMUIR-BLODGETT FILMS*

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In angle-scanned photoelectron diffraction (PD) from molecules adsorbed on surfaces, it is known that intra-molecular photoelectron forward scattering can produce peaks at angles which coincide with the orientations of axes connecting near-neighbor atoms. Thus, this technique has proven useful for determining the orientation of simple molecular species adsorbed on surfaces, e.g. CO/Ni(001).¹ We have carried out a feasibility study in which we applied this technique for the first time to the study of Langmuir-Blodgett (LB) films on Si wafers. 1- and 3-layer Cd stearate and 1-layer Mn stearate samples were measured. The molecules comprising these films contain an 18 atom C 'zigzag' chain. Forward scattering along the chain axis and between nearest-neighbor C atoms is likely to produce PD peaks at angular positions which are directly related to the molecular tilt angle and the azimuthal orientation of the C zigzag.

The photoelectron diffraction function χ , defined as

$$\chi = (I - I_0)/I_0, \quad (1)$$

was measured as a function of the polar emission angle θ for a photon energy of 450 eV. I and I_0 represent the C(1s) angle-resolved photoemission peak intensities from the LB film and from a powder reference sample, respectively. Count rates were adequate to perform the experiments in a reasonable time as, e.g., 5000 cps were obtained on the C(1s) peak with a ≈ 3 eV analyzer energy resolution. However, the uv beam was found to degrade the LB films on the time scale of several hours, requiring frequent sample changes.

A strong 20% oscillation in χ was obtained from the 3-layer Cd stearate sample (Fig. 1). Peaks occur for χ approximately equal to 0°, 40°, and 50°. The first may have a simple interpretation involving forward scattering along the axis of the LB molecule, while the peak at 40° may be associated with forward scattering along nearest-neighbor C atoms. Theoretical calculations of the polar PD pattern are planned to test this interpretation and to attempt to extract the molecular tilt angle with respect to the surface. We did not observe PD patterns from the 1-layer LB films, possibly due to sample quality.

We intend to extend this work involving systems with one or a small number of organic long chain layers to study different molecular species and the effect of different sample preparation conditions.

Fig. 1. C(1s) polar photoelectron diffraction pattern obtained from a 3-layer Cd stearate LB film, for a photon energy of 450 eV.

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*Work performed under the auspices of the U.S. Department of Energy, under contract No. DE-ACO2-76CH00016.

PHOTOEMISSION INVESTIGATION OF THE $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ HIGH TEMPERATURE SUPERCONDUCTORS

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A series of resonance photoemission and photon stimulated desorption measurements were made on the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ high temperature superconductors. Five samples were used, with $x=0, 0.1, 0.15, 0.2$ and 0.3 . The best stoichiometry for high temperature superconductivity is $x=0.18$, which has a T_c of about 40K.

The experiments were performed at room temperature in UHV using beamline U14. The surfaces were prepared by scraping with a ruby stone rod. A typical valence band spectrum is shown in Figure 1. A freshly scraped surface was found to degrade relatively quickly in the UHV environment, with the valence band peak degradation intensity near the fermi level within 20-30 minutes. Calculations [1] indicate that the valence band peak is composed primarily of copper and oxygen contributions, with oxygen states dominating the lower binding energy region of the peak. Thus we attribute the degradation shown in Figure 1 to a loss of surface oxygen from the material. The peak below the valence band at about 10eV binding energy is a contamination peak due to surface oxygen and carbon.

Figure 1

Figure 2.

A striking feature of photoemission from rare earth compounds is the resonance behavior at the 4d threshold. Various CIS and CFS (constant initial state; constant final state) spectra from La_2CuO_4 are shown in Figure 2. Three resonance features are observed: two sharp peaks below the 4d threshold at 97.8eV (not shown) and 102.2eV respectively, and a large feature centered at 118eV. Little variation in these spectra was observed between differing stoichiometries. The curves shown in Figure 2 are almost identical in form to those measured from LaB_6 [2]. The resonances are attributed to transitions to empty 4f states: the strong exchange interaction between the excited 4f electron and the 4d hole produces highly localized "atomic like" 4f levels which give rise to the resonance features in Figure 2 [2].

Figure 2 shows CIS scans which illustrate the resonant enhancement of the La 5p peak and the valence band due to a direct recombination decay of the excited 4f electron. The 5p emission shows a strong enhancement at 118eV (similar to the CFS) while the valence band is only weakly enhanced, also similar to the LaB_6 data [2]. This indicates that while the major contributors to the valence band are Cu and O [1], lanthanum electrons contribute a small but significant intensity.

Photon stimulated desorption spectra were obtained via a time of flight technique. The only desorbing ionic species detected at the various La, Sr, Cu and O edges was H^+ . The lack of O^+ or OH^+ desorbing ions indicates that the loss of surface oxygen is not due to the impinging photon beam. Strong "prompt" fluorescence signals were also detected, presumably from desorbing excited hydrogen.

This work was sponsored by the DOE under contract DE-ACO2-76CH00016.

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TITLE OF EXPERIMENT: Large Area X-ray Multilayer Mirror Calibration DATE: June 7-17, 1987

EXPERIMENTERS: Leon Golub (Harvard-Smithsonian Ctr. for Astrophys.) and Eberhard Spiller (IBM's Thomas J. Watson Research Center)

ABSTRACT

The soft X-ray reflectivity of a 25cm diameter Ritchey-Chrétien telescope was measured, using the U14A monochromator. Both X-ray throughput and absolute wavelength of peak reflectivity were determined and compared with measurements performed on "witness" samples. The latter consisted of small Si wafer strips which were glued to the surface of the figured optics and coated at the same time.

The telescope is a two-mirror Cassegrain-type system, in which the overall performance depends upon the quality of the multilayer coating on each mirror (uniformity, boundary roughness, accuracy of 2d-spacing), as well as on the degree of overlap between the passbands of the two mirrors. Much of our testing has been done with the witness mirrors, and the primary purposes of the NSLS tests were: i) to determine whether the telescope mirrors have on their surfaces the same coatings that were deposited onto the witness samples, ii) to establish that the optical system will transmit X-rays of the predicted wavelengths from the entrance aperture to the focal plane; and iii) to determine the X-ray reflectivity and wavelength of peak throughput of the telescope. All of the above measurements need to be accurate to $\ll 1.3\%$, which is the multilayer passband; this translates to an absolute accuracy of $\ll 1.0$ eV.

The major result is shown in the figure below, which indicates that the mirrors and the witness samples both received the same coating to within ± 0.2 eV. The absolute reflectivity is more difficult to determine due to enlargement of the transmitted image relative to the straight-through; however, we calculate that the U14 measurement agrees to within 25% with measurements performed on the samples.

Fig. 1. Measured throughput of the X-ray telescope at output of the U14A monochromator

This work was supported by the NSF under Grant DMR-8313070 to the Smithsonian Institution.

ANGLE-RESOLVED AND RESONANT PHOTOEMISSION STUDIES OF MnO AND Fe₃O₄

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Although angle-resolved photoemission has proven to be a powerful technique for mapping out the bulk and surface electronic structures of a large number of metals and semiconductors, very few angle-resolved measurements have been performed on transition-metal oxides. This is partly due to the fact that the valence band features of the oxides are generally quite broad, making the determination of band dispersions difficult. Nonetheless, we have carried out angle-resolved normal emission experiments on cleaved single crystals of MnO and Fe₃O₄ and have qualitatively determined the energy dispersion of the valence band. In addition, the 3d character has been distinguished from O 2p derived valence band features by using constant-initial-state (CIS), constant-final-state (CFS), and total yield measurements, taken with photon energies at the 3p-3d resonance [1].

The photoemission spectra were acquired on beamline U14 at NSLS using photon energies between 30 and 120 eV. Normal emission spectra were measured with a hemispherical analyzer at $\pm 2^\circ$ angular resolution, and CIS and CFS spectra were taken in the angle-integrated mode using a cylindrical mirror analyzer. The single crystals were oriented to expose MnO (100) and Fe₃O₄ (110) faces, and they were cleaved in situ at $< 2 \times 10^{-10}$ Torr.

MnO is an insulating monoxide, in which the 3d⁵ electrons are believed to be fairly localized on the Mn²⁺ ions due to electron correlation effects. Normal emission spectra taken from MnO (100) for $30 < h\nu < 80$ eV exhibit two peaks separated by 1.8 eV due to excitation from the $e_g^\uparrow$ and $t_{2g}^\uparrow$ orbitals in the Mn²⁺ ($t_{2g}^3 e_g^2; ^6A_1$) ground state. A primarily O 2p region is located between 1 and 5 eV above the $t_{2g}^\uparrow$ peak, and a satellite feature appears near 7 eV; spectra are arbitrarily referenced in energy to the $t_{2g}^\uparrow$ peak because the location of the Fermi level within the bandgap could not be determined due to surface charging. Of interest in a normal emission experiment are peak dispersions. Fitting Gaussians to the $t_{2g}^\uparrow$ and $e_g^\uparrow$ peaks, we find that these Mn 3d derived states do not disperse more than ± 0.1 eV relative to each other. In contrast, features in the O 2p region do show some dispersion, although band mapping is tenuous because of the broad nature of the peaks. These data support a localized 3d electron view of the electronic structure [2,3], although a one particle band theory [4] showing very little dispersion cannot be ruled out. 3p-3d resonance effects are visible in the normal emission data at photon energies between $48 < h\nu < 52$ eV. The $t_{2g}^\uparrow$ and $e_g^\uparrow$ peaks undergo an antiresonance as the photon energy is swept through the Mn 3p photo-threshold, whereas emission in the O 2p and satellite regions exhibits resonant behavior. The associated Fano-like lineshapes are clearly evident in CIS and CFS spectra. The antiresonance of the lowest binding energy Mn 3d features is attributed to screening of the final states by ligand-to-metal charge transfer [5]; the satellite is believed to correspond to an unscreened 3d⁴ final state. A resonant enhancement in the O 2p region suggests some overlap of the Mn 3d and O 2p final states.

Fe₃O₄ crystallizes in the spinel structure, which contains Fe²⁺ and Fe³⁺ ions coordinated in octahedral and tetrahedral sites of an fcc lattice of O²⁻ ions. It exhibits metallic conductivity at room temperature, and the electronic structure can more justifiably be described by itinerant electrons. Normal emission spectra measured from cleaved Fe₃O₄ (110) between $34 < h\nu < 80$ eV are composed of many multiplet lines from the Fe²⁺ and Fe³⁺ ions, which are difficult to separate from the overlapping O 2p band. CIS and CFS spectra at the 3p-3d resonance reveal that the main valence band emission is well screened by ligand charge transfer; the intensity of the unscreened satellite peak is very weak. An analysis of the data in terms of a strictly one electron band approach, and a comparison to band calculations [6], is in progress.

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Note: The authors gratefully acknowledge assistance by K.E. Smith and the NSLS staff.
This work was partially supported by NSF, Solid State Chemistry Grant No. DMR-8202727.

ENERGY-DEPENDENT PHOTOELECTRON DIFFRACTION FROM GaAs(110)*

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Energy-dependent photoelectron diffraction (EDPD) has developed into a useful surface structural tool, so far employed primarily as a means of determining site types and z displacements in ordered overlayer systems.¹ The present study was conducted to test whether EDPD could accurately determine the structural parameters associated with the GaAs(110) surface. This is a considerably more complex problem, first because the surface reconstructs, and second because atoms (either Ga or As) in many different local environments contribute simultaneously to the diffraction pattern. A further motivation for studying this system is the uncertainty which has existed in the exact nature of the reconstruction due to the inability of low energy electron diffraction (LEED) to accurately determine the displacements of atoms parallel to the surface.²

The measurement of EDPD involves determining the function $\chi(h\nu) = [I(h\nu) - I_0(h\nu)]/I_0(h\nu)$, where $h\nu$ is the photon energy, and I and I_0 represent core level angle-resolved photoemission peak intensities with I_0 corresponding in principle to the case where there is no scattering of the outgoing photoelectron wave from its neighbors following the initial excitation. In this study we measured the Ga(3d) core level for $h\nu$ between approximately 100 and 280 eV (for a photoelectron kinetic energy between approximately 77 and 257 eV). $I(I_0)$ is then the Ga(3d) peak area following subtraction of an integral background. I_0 was measured from a GaAs reference sample with a disordered surface showing no LEED pattern. Use of a reference sample also has the advantage that it normalizes out the dependence of the peak intensity on factors such as the monochromator function, beam current decay, beam movement (on a long time scale), and analyzer transmission function. EDPD curves were obtained at eight near-grazing (within 20° of the surface) emission angles to enhance surface sensitivity. The full range oscillation in $\chi(h\nu)$ ranged from approximately 15% to 50%. Figure 1 shows the results obtained at a polar emission angle (wrt the surface) θ of 20° and an azimuthal emission angle of 180° (90° from the mirror plane).

Fig. 1. Experimental energy-dependent photoelectron diffraction curve obtained 20° from the surface and 90° from the surface mirror plane.

Structural information is derived from the experimental data through comparison with theoretical EDPD curves computed assuming different values for the various structural parameters. To date, we have carried out calculations in the somewhat crude plane wave (PW) and single scattering (SS) approximations. The results show both an encouraging level of agreement with experiment and a high degree of structural sensitivity, although the latter is strongly dependent on emission angle. It thus appears likely that in conjunction with more accurate calculations to be carried out, the EDPD results will provide an accurate structural determination of the GaAs(110) surface.

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*Work performed under the auspices of the U.S. Department of Energy, under contract No. DE-ACO2-76CH00016.

RESONANT PHOTOEMISSION EFFECTS AND BULK BAND DISPERSION IN Ti_2O_3 AND V_2O_3

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The bulk electronic structure of Ti_2O_3 and V_2O_3 has been the subject of considerable experimental and theoretical investigation over the last forty years, motivated primarily by a desire to understand the nature of the metal-insulator transitions which these materials undergo [1,2]. We report here results of a comprehensive study of the electronic structure of Ti_2O_3 and V_2O_3 using both angle integrated and angle resolved ultraviolet photoemission spectroscopy (ARUPS) performed on NSLS beamline U14A [3].

Ti_2O_3 and V_2O_3 cleave along only one direction, exposing the (10 $\bar{1}$ 2) surface [4]; all the experiments reported here use single crystal samples cleaved in UHV. Angle integrated photoemission spectra were obtained from V_2O_3 at various photon energies. These spectra are similar to those obtained previously using a He discharge lamp [4]; close to the Fermi level, E_F , emission from the V 3d states is observed and below this lies the broad emission from the O 2p band. However there is a feature visible in the spectra which was not seen in the previous study [4]. The binding energy of this feature, 10.8 eV, coincides with a bulk energy loss observed in the electron energy loss spectrum of V_2O_3 [5] and thus we can identify this feature as a valence band satellite according to the exciton model of de Boer et al. [6]. The V 3d emission displays a resonance behavior close to the V 3p - 3d threshold [7]. However the onset of the resonance is delayed by 6 eV above the V 3p 3d separation; in V metal the delay in resonance is almost 8 eV [8].

Normal emission ARUPS spectra were taken from both the cleaved Ti_2O_3 (10 $\bar{1}$ 2) and V_2O_3 (10 $\bar{1}$ 2) surfaces. In general the ARUPS spectra were quite similar to those obtained in an angle integrated mode [4,9]. The direction in k-space probed in a normal emission experiment from a (10 $\bar{1}$ 2) surface in a corundum structured crystal is not of particularly high symmetry; none of the available band structure calculations provide dispersion curves for the direction studied in these experiments [10,11]. However, the directions along which the calculations were made do intersect the experimentally probed line at a number of points where comparison with the experiment can be made. The normal emission spectra obtained from Ti_2O_3 (10 $\bar{1}$ 2) show a small (<0.4 eV) but significant dispersion for the Ti 3d states near E_F . Similarly the V 3d emission in ARUPS spectra from V_2O_3 (10 $\bar{1}$ 2) shows a slight dispersion (<0.3 eV) [3]. The observed dispersion in both materials shows little similarity to that expected from the calculations. However, this does not necessarily invalidate the calculations since the dispersion occurs in the photon range where resonant photoemission is the dominant contribution to the measured 3d intensity. The onset of resonance is delayed in the case of Ti_2O_3 just as it is in V_2O_3 .

Acknowledgements

The authors wish to acknowledge the invaluable assistance of R.J. Lad and the staff at NSLS, in particular R.F. Garret, E. Kneedler, M.J. Sagurton and G.P. Williams. This work was partially supported by NSF Solid State Chemistry Grant DMR 82-02727.

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NEAR-EDGE X-RAY ABSORPTION FINE-STRUCTURE OBSERVATIONS OF ORDERING AND METALLIC-LIKE BEHAVIOR IN ORGANIC CONDUCTING POLYMERS ON Pt.

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We observed a remarkable ordering of films of several layers thickness of poly(3-methylthiophene) electrochemically deposited on a Pt electrode, using NEXAFS.¹

Polythiophene and its derivations represent a new class of organic conducting polymers which are of great interest for two reasons. First, their electrical conductivities can be varied by 12 orders of magnitude by doping, and secondly, they show great chemical and electrochemical stability against moisture and oxygen.² Neither the conduction mechanisms or the morphology of these materials are known. Our NEXAFS measurements sought to address the unoccupied electronic structure questions from peak heights and positions and the physical structure issue from the polarization dependence.

The figure below shows polarization dependent data for undoped poly(3-methylthiophene). A strong transition at grazing incidence was observed for peak A which we assign to a $2\pi^*$ final state, which indicates that the thiophene ring is lying down on the surface.

Polarization dependence of NEXAFS spectra obtained from a 20-Å-thick film of undoped poly(3-methylthiophene) above (a) the C K edge and (b) the S L edge. The insets indicate the direction of poly(3-methylthiophene) film.

On doping with ClO_4^- , we saw essentially the same features with no significant changes in the σ resonances. This suggests that no modifications to the basic structural unit in this polymer took place during the doping process. However, the $2\pi^*$ band was substantially affected with a decrease in intensity of the main $1s \rightarrow 2\pi^*$ transition and the appearance of additional intensity at low energy (282-284 eV) above the carbon edge. We associate these modifications with the formation of empty states in the gap which is consistent with UPS and XPS³ studies.

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CORE ELECTRON EXCITATION AND RELAXATION IN MOLECULES*

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Our research program is directed at learning about the chemical consequences of core electron excitation in molecules. With tunable, monochromatic synchrotron radiation, it is possible to excite selectively not only core electrons of different elements, but also core electrons of the same element in different chemical environments in the molecule. In addition, different types of excited states can be prepared. The core electron can be excited to unoccupied valence orbitals, Rydberg orbitals, shape resonances, or the ionization continuum. Auger decay, accompanied by fragmentation of the molecule, usually occurs following such excitation in the gas phase. It is our objective to learn how and why the fragmentation varies with molecular structure and depends upon the nature of the core hole excited state. The techniques of photoelectron, mass, and fluorescence spectroscopy are being used in these studies. Analysis of data obtained for carbon monoxide and trifluorotoluene almost is completed. Recently data has been collected for water, methanol, propanol, diethylether, methane, and tetrafluoromethane. Other results are summarized below.

For nitrous oxide, core holes were created selectively in either of the two nitrogen atoms or in the oxygen atom by exciting a 1s electron to an unoccupied valence orbital. Time of flight mass spectroscopy was used to elucidate the chemical consequences of this excitation. Clear changes in the mass spectra with the atomic site of excitation were observed. These changes can be understood qualitatively in terms of the atomic populations, which govern the Auger decay channels, and the overlap populations, which determine the bond structure, of the valence molecular orbitals.

Mass spectra also were obtained to characterize the fragmentation of acetone following excitation of an oxygen 1s electron to an unoccupied valence orbital, to a shape resonance, and to the ionization continuum. The production of methyl ion fragments was found to exhibit a marked enhancement that appears to be linearly related to the oxygen 1s partial absorption cross section. Neither carbon nor oxygen ions are significant products of oxygen 1s excitation. These results are intriguing because while localized Auger decay and bond rupture around the site of the core hole would explain the formation of C^+ and O^+ , the production of methyl ions may be consistent with the molecular orbital population analysis used for the case of nitrous oxide.

Fluorescence spectra can be used to detect neutral fragments and ions produced in electronically excited states by Auger decay of core holes. The most interesting results have been obtained for the case of oxygen. The luminescence spectrum obtained following excitation in the region of the oxygen K edge consists of two series of bands, one in the blue region (400 to 500 nm) and the other in the green region (500 to 700 nm). It was found that ion yield spectra and the relative intensity of these bands vary with excitation energy through the pi and sigma resonances. The green bands clearly correspond to the first negative system of O_2^- . The blue bands, however, do not match known luminescence of this ion or other possibilities. Recent calculations, and data from electron impact and double charge transfer experiments indicate that there are two states of O_2^{++} separated by 3 eV. The blue bands therefore may be due to O_2^{++} . This is an exciting result because there is only one previous report of dispersed luminescence from a doubly charged molecular cation in the literature. Probing the Auger final state by observing its fluorescence decay makes it possible to do Auger spectroscopy with the high resolution of an optical spectrometer. Such luminescence spectra with resolved rotational and vibrational structure can provide significant information about the energy spacing between electronic states, about the structure and bonding properties of ions in these states, and about the populations of rotational and vibrational levels, which can characterize the populating mechanisms.

A theory, based on the concept of orbital force, is being developed to explain or predict fragmentation patterns of polyatomic molecules following the multiple electron excitation and ionization that accompanies decay of a core hole. A change in the valence electron configuration produces a stress on the atoms in a molecule. This stress is relieved by changes in bond lengths and angles, by electronic relaxation, and by bond rupture. An analysis of this stress may serve to identify the bonds that rupture. To date, this theory has been tested on diatomic molecules and ions. It has successfully correlated bond lengths and vibrational force constants of different excited electronic states.

* This research is supported by the National Science Foundation, Grant CHE 8703340.

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DEFECT GENERATION IN SILICON DIOXIDE FROM SOFT X-RAY SYNCHROTRON RADIATION

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X-ray lithography is one method being investigated to pattern the next generation of semiconductor devices because of its high resolution capabilities, i.e. short wavelength. To take full advantage of this high resolution capability, the X-ray source must produce a very intense collimated beam. One such source is the vacuum ultraviolet (VUV) storage ring of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Such a ring provides a continuum of photon energies from less than 10 eV to above 5000 eV. It has been reported that X-ray radiation at energies above 1 KeV produces fixed positive charge, fixed negative charge, neutral electron traps in device gate insulators such as SiO₂ in large numbers.¹⁻⁶ The present report describes preliminary studies on defect generation in SiO₂ from exposure to monochromatic X-ray radiation in the energy range from 300 to 1000 eV. The purpose of these studies was to determine if energy threshold(s) exist below which one or more of the three major electrically active defects (fixed positive charge, fixed negative charge, and neutral electron traps) are not generated, or where the number generated for a given number of rads begins to decrease monotonically with decreasing energy. If such a threshold exists, the energy used for X-ray lithography could be tailored such that little or no oxide damage occurs during the exposure. The alternative is to use energies that will generate the damage and 1) try to stop the X-rays from reaching the oxide by using a trilayer photoresist technology, or 2) attempt to anneal the damage after the exposure.⁶ The analyses are based on the results of experimental studies in which the gate insulators in insulated gate field effect transistors were exposed to the monochromatic X-rays at the NSLS U15 beamline and then measured using an optically assisted hot electron injection technique.⁸ The exposures were done for 1) a constant incident energy of 120 mJ/cm² to simulate an X-ray lithographic step, and 2) constant absorbed dose of 2x10⁷ rads (SiO₂) to determine the energy dependence of the defect generation. To uniformly expose a number of devices, the samples were scanned vertically through the X-ray beam. Since the X-ray beam has a near gaussian distribution in the horizontal direction, only devices at the same horizontal position (same column) receive the same dose. Devices on the sample that were to receive a different energy exposure, or that were to receive no radiation (controls) were shielded by stainless steel plates. In using the beamline, care must be taken in determining the actual exposure, because heating of the torodial grating monochromator by the incident "white" radiation from the synchrotron ring can reduce its efficiency, i.e. the actual photon flux incident on the sample may not be proportional to the beam current in the ring. The results indicate that the generation of fixed positive charge, fixed negative charge, and neutral electron traps remains approximately constant with decreasing X-ray energy. At 2x10⁷ rads, using a special test device,⁶ the number of generated fixed positive charges was approximately 9x10¹¹ cm⁻², the number of fixed negative charges was 4x10¹¹ cm⁻², and the number of neutral electron traps was 1.7x10¹² cm⁻². If X-ray lithography is used to pattern a metal layer, the maximum temperature that can be used subsequently to anneal the damage created is approximately 400°C. The results obtained here indicate that such annealing temperatures reduces the number of defects to approximately 3.5x10¹¹ cm⁻² neutral electron traps, 1x10¹¹ cm⁻² fixed positive charge, and less than 1x10¹⁰ cm⁻² fixed negative charge.

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TEMPERATURE DEPENDENCE OF LOCAL ENVIRONMENT
SURROUNDING OXYGEN ATOMS IN Y-Ba-Cu-O COMPOUNDS

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The recent discovery of superconductivity in oxides with unprecedented high transition temperatures has stimulated enormous interest in the study of various physical properties of these materials. Although the underlying mechanism responsible for the high transition temperature remains unclear, it is conceivable that structural instabilities, lattice defects, oxygen vacancies, local atomic environment may play an important role in effecting the superconducting state. In the present work, we have investigated the local structure around the oxygen atoms in a high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by using the EXAFS technique, which provides information on the bond length and disorder between the oxygen and Cu/Ba atoms. Our results indicate a structural instability transition around 161K not reported before.

Using the EXAFS spectra, we have extracted the effective Debye-Waller parameter σ as a function of temperature, which is plotted in Fig. 1. An abrupt change in σ was observed at a transition temperature around 161K. This can also be observed more directly by inspection of the k-value of the maximum amplitude of the backtransform oscillations, which shows an abrupt change at 161K. Other than this abrupt change, we see little variation in σ as a function of temperature. This suggests that our sample most likely contains a large number of defects, and the static disorder in the system masks the usual temperature variation of σ as predicted by the Einstein model of lattice vibration.

In summary, we have investigated the local short-range-order structure around the oxygen atoms in the high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by using the EXAFS technique. Our findings indicate that the material contains a high degree of disorder and undergoes a structural transition as the temperature is lowered through 161K, seen as an increase in the effective Debye-Waller factor.

This work is supported in part by the Department of Energy.

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Figure Captions

Fig. 1 -- Temperature dependence of the effective Debye-Waller factor σ .
(a) O-Cu bond, (b) O-Ba Bond.

INTERFACIAL ROUGHNESS OF InAs/GaAs HETEROSTRUCTURES
DETERMINED BY X-RAY REFLECTIVITY

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Many important physical properties of quantum-well systems are strongly related to the material structure at the boundary between different layers; the understanding and control of the interface appear to be essential for further development and device applications of the multilayer and single layer heterostructures. Despite extensive studies of the transport and optical properties of these layered structures, little is known at the present time about the interfacial roughness. This slow progress is due to lack of efficient experimental techniques for probing the interfacial structure, especially for nondestructive characterization of interfaces beneath the top surface of as-made samples.

We have measured the reflection of monochromatic x-rays by an InAs/GaAs heterostructure. The heterostructure was produced by growth of a thin layer of InAs on GaAs by molecular beam epitaxy (MBE), with a nominal layer thickness of 250 Å estimated from growth time.

Our data show regular oscillations in both the reflectivity and wavelength-modulated reflectivity as a function of grazing angle. These oscillations are due to interfacial effects and contain information about the layer thickness and interfacial roughness. This information can be extracted by comparison of our data with a theoretical calculation based on the well-known Fresnel equations, modified to include surface roughness via a scalar scattering theory in the long wavelength regime.^{1,2,3} We have found good agreement between the theory and our data, as can be seen in Figure 1. From the fit of the theory to our data, we have determined the thickness as 248 ± 6 Å, the InAs-GaAs interfacial roughness as 18 ± 5 Å, and the top surface roughness as 1 Å or less.

In conclusion, our results indicate that a layer of InAs on GaAs grown by MBE has started from a rough surface and ended with a smooth finish. In performing this experiment we have demonstrated the utility of this practical technique for nondestructive evaluation of the interfacial roughness in semiconductor heterostructures. This work is supported by ONR.

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Figure Captions:

Fig. 1. -- Reflectivity from an InAs/GaAs heterostructure for 442.1 eV x-rays, with the measured data plotted as points and a calculation plotted as a curve. The parameter values used for the calculation were: $d = 255$ Å, $\sigma_1 = 0.40$ Å, $\sigma_2 = 17.5$ Å.

SECTION 3

REPORTS OF THE X-RAY RESEARCH AT THE NSLS

This section contains the reports of research carried out at the NSLS X-ray storage ring during the 1987 fiscal year. Most of the contributions have been specifically written for this annual report by the experimenters. Their efforts are greatly appreciated by the annual report staff. The reports are presented by beam line and are arranged alphabetically by first author (except where a specific order was requested.) The Table of Contents that follows is also arranged by beam line and first author.

X-Ray Storage Ring Parameters as of June 1987	
Parameters	X-Ray Storage Ring
Normal Operating Energy	0.75 - 2.5 GeV
Design Current	0.5 amp ($1.9 \times 10^{12} e^-$)
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 6.0 T (W)	0.50 Å (25 keV)
$B(\rho)$	1.22 Tesla (6.875 meters)
Electron Orbital Period	567.7 nanoseconds
Damping Times (0.7 GeV)	$\tau_x = \tau_y = 6 \text{ msec}; \tau_z = 3 \text{ msec}$
Touschek (0.7 GeV, 1A)	$\geq 0.6 \text{ hrs}$ ($v_{RF} = 800 \text{ kV}$)
Touschek (2.5 GeV, 0.5A)	$\geq 8 \text{ hrs}$ (same)
Lattice Structure (Chasman-Green)	Separated Function, Quad, Triplets
Number of Superperiods	8
Magnet Complement	16 Bending (2.7 meters each) 40 Quadrupole (0.45 meters each) 16 Quadrupole (0.80 meters each) 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	252 kW/0.5 amp of Beam
R.F. Peak Voltage	800 kV
Design R.F. Power	500 kW
ν_s (Synchrotron tune)	0.002
Natural Energy Spread (σ_ϵ/E)	8.2×10^{-4}
Natural Bunch Length (2σ)	10.5 cm
Horizontal Damped Emittance (ϵ_x)	8.0×10^{-8} meter-radian
Vertical Damped Emittance (ϵ_y)	8.0×10^{-10} meter-radian
Power per Horizontal milliradian, 0.5A	40 watts
Source Size: σ_h, σ_v	$\sim 0.35 \text{ mm}, \sim 0.15 \text{ mm}$

Source of Data: NSLS Parameters, January 1983, compiled by A. van Steenberg; updated values provided by Ben Craft (NSLS).

RESEARCH REPORTS FOR THE X-RAY BEAM LINES

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VIBRATIONAL STRUCTURE IN THE AUGER DECAY OF CORE EXCITED N₂

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We have studied the effects of nuclear motion on the Deexcitation electron spectrum of N₂, C₂H₂, and CO₂ resulting from the Auger-like decay of a neutral core to bound state excitation into single hole final states. Here we want to report the results for N₂. The initial $1s + 1\pi_g$ core excitation of N₂ was accomplished using quasi-monochromatic radiation from the soft x-ray undulator on the X17T beamline. The $1\pi_g$ core excited state has a lifetime of 10^{-14} sec which is comparable to the vibrational period of the N₂ molecule. This state undergoes an Auger type decay to the $3\sigma_g^{-1}$ and $1\pi_u^{-1}$ single hole final states. The resulting spectrum is shown in Fig. 1 (labelled DES) with the $1\pi_u$ single hole final state peaked at 17 eV binding energy while the $3\sigma_g^{-1}$ final state shows a broad vibrational sequence.

This deexcitation lineshape depends upon the electronic matrix elements for the excitation and decay process and the product of vibrational matrix elements from the initial state to the intermediate core excited vibrational states times the element from the intermediate state to the final vibrational state. The vibrational structure is modulated by the time evolution of the core excited state before it decays and interference effects result from the two step nature of the process. This is in contrast to a photoemission event which leads to the same single hole final states in a one-step process. The corresponding photoelectron spectrum is shown in the top part of Fig. 1 (PES).

Using a simple Franck Condon analysis^{1,2} with a complete decoupling of the Auger and vibrational matrix elements, we were able to reproduce the deexcitation spectrum very well. This leads to the conclusion that despite the short lifetime of the core excited state, the vibrational structure is dominated by the overlap between the core excited vibrational state and the final vibrational state. The $1\pi_u^{-1}$ intensity falls into one transition. Similarly, the broad $3\sigma_g^{-1}$ vibrational structure can be explained by the large change in equilibrium nuclear spacing in this transition. We find that the interference term for the two step deexcitation process plays a minor role in determining the vibrational substructure.

The deexcitation vibrational structure is compared to that seen in direct photoemission in Fig. 1. Here the classical argument for the large vibrational structure in the $1\pi_u^{-1}$ final state is simply that a large change in equilibrium bond length has occurred directly from the initial to the final state when the bonding $1\pi_u$ electron is ejected. The $3\sigma_g$ photoemission hardly causes any bond length change and thus appears as nearly one peak. These type of experiments involving extremely short-lived intermediate states open up the possibility to study the dynamical processes and energy dissipation in a new, sub-picosecond time regime. The interference processes, which will be more prominent if the timescale gets even shorter, i.e. for similar decay processes in molecules composed of atoms with a larger Z, allow for a test of quantum mechanics at a very fundamental level. These studies were carried out at the X17T spectroscopy beamline at the NSLS. This experimental program is partially supported by NSF under grant #NSF-DMR-851919.

Fig. 1 Photoemission spectra (taken from A.L. Gardner and J.A.R. Samson, J. Chem. Phys. 62, 1447 (1975)) in top panel and Deexcitation Electron spectrum of N₂ in the bottom panel. The electron spectra are shown on a binding energy scale and the emission observed corresponds to the creation of the $3\sigma_g^{-1}$ ($X^2\Sigma_g^+$) and $1\pi_u^{-1}$ ($A^2\Pi_u$) states of N₂⁺.

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The sol-gel transition of gelatin in solution (0.1 M NaCl, pH 7) with concentrations varying from 0.5% to 22% was investigated by means of small angle X-ray scattering (SAXS). Gelatin solutions were quenched from 50°C (sol) to 11°C with the gelatin temperature measured at 30°C using optical rotary dispersion. Figure 1 shows typical time-resolved scattering patterns of the gelatin sol-gel transition using 0.5% gelatin in 0.1 M NaCl and a temperature jump from 50°C to 10.9°C. The scattering curves represent a growth of scattered intensity, especially at small scattering angles as a function of time. After quenching, the scattered intensity remained relatively weak until the sample temperature reached about 30.7°C. Each curve was measured for a period of 100 seconds. The bottom curve represents a composite scattering curve with temperatures varying from 30.7 to 13.6°C. The next composite scattering curve from the bottom represents a temperature variation from 13.6°C to 11.4°C over the 100-second period. The remaining curves (third curve from bottom to top curve) are at 10.9°C. If we denote the bottom curve as the starting time, the time sequence for the eight representative curves (from a total of 30) is 0, 100, 400, 900, 1400, 1900, 2400, 2900 seconds.

The details of the scattering curves will be analyzed in terms of fractal dimension and in combination with light scattering and small angle neutron scattering data.

Figure 1. Sol Gel Transition of Gelatin.

The crystallization behavior of blends of high and low density polyethylene (PE) was investigated using time-resolved small angle x-ray scattering (SAXS). Crystallization processes of high density PE, low density PE and 50:50 HD/LD PE were studied as follows: (1) slow cooling of the samples from the melts to near the crystallization temperatures, (2) isothermal crystallization using temperature jumps from 135°C to 110°C for HDPE, and from 109°C to 99°C for LDPE, and (3) quenching of samples from $T > T_g$ to $T \ll T_g$. Separate crystallization phenomena were observed.

Figure 1 shows typical SAXS curves of slow cooling of 50:50 HD/LD PE (cooling rate = $0.3^{\circ}/\text{min}$). By comparing the scattering curves with those obtained from HDPE and LDPE, we can deduce the crystal growth process and its origin, which cannot be obtained by standard SAXS measurements.

The details of the crystallization process for HDPE/LDPE polymer blends will be studied using the existing HDPE, LDPE and 50:50 LDPE/HDPE blend samples at different temperature jump distances from the crystallization temperatures in order to reduce the rate of crystallization.

Figure 1. Typical SAXS curves of slow cooling of 50:50 HD/LD PE (cooling rate = $0.3^{\circ}/\text{min}$).

The fractal dimension d_f of a branched epoxy polymer (DGEb) before its gelation point has been measured by small-angle x-ray scattering. The fractal dimension ($d_f = 2.17$ using a molar ratio of epoxy (DGEb):curing agent (CH):catalyst (CA) = 1:2:0.001 at 80°C) could be used to provide a new description of the structure of epoxy polymers as well as additional macromolecular information on the kinetic process.

From our SAXS results, we can draw the following conclusions:

1. We can use SAXS to determine d_f which is related to the epoxy polymer structure.
2. Before the gel point, we can determine M_w , R_g using static scattering techniques. With d_f the molecular weight distribution at each stage of the polymerization process can be obtained experimentally from dynamic light scattering, especially in view of the fact that the particle scattering factor in the visible range for such epoxy systems is near unity.
3. Beyond the gel point, we can use fractal dimension to investigate changes in epoxy structure.

A detailed study of the structure and dynamics of this epoxy model system using a combination of SAXS and light scattering is underway.

SYNCHROTRON RADIATION STUDY OF THE FIVE-DIMENSIONAL, MODULATED PHASE OF TTF-TCNQ AT 15K. P. Coppens, D. Levendis, A. Paturle, V. Petricek, Gao Yan (SUNY/Buffalo) and F.K. Larsen (U. of Aarhus, Denmark).

The one-dimensional conductor TTF-TCNQ (tetracyanoquinodimethanide-tetrathiofulvalene) undergoes a Peierls transition at 53K and further transformations at 49 and 38K. Though the modulation vectors have been determined and the average structure is known at 45K (1), detailed information on the molecular displacement has been lacking. The scarcity of experimental information is due to the weakness of the satellites which are typically 10^{-4} times the intensities of the main reflections.

With the synchrotron source we have measured a total of 564 reflections, including 450 satellite reflections with $\sin\theta/\lambda$ in the range of $0.2-0.5\text{\AA}^{-1}$. Satellite intensities on an absolute scale were obtained by scaling the main reflection intensities to F^2 values calculated from the 45K parameters (1). 137 unique satellite intensities with $I > 30$ were used in the least squares refinement in the five-dimensional centrosymmetric super-space group $P:P2_1/c:cmm$. Equations for the displacements of symmetry-related atoms in the five-dimensional case will be given elsewhere. A new computer program, JANA5, was used. We assumed, as in our previous work (2), that the molecules are displaced as rigid bodies by the modulation wave. This assumption greatly reduces the number of parameters to be determined.

The final R-value for 137 satellite reflections is 0.198. The main feature of the $2k_F$ modulation is a translational displacement of the TTF molecules. The largest magnitude, for the q_2 translational wave of TTF is $0.0191(8)\text{\AA}$ (Figure 1). All other translations, though experimentally significant, are smaller than $0.01\text{\AA}$. The rotations are less than 0.2° . The direction of the main translational displacement is within experimental error along the long molecular axis of both molecules. The largest atomic displacement under these modes is only about $0.003\text{\AA}$.

A most curious result is that different stacks distort in different ways, thus creating a band gap which is different for chemically equivalent columns.

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Figure 1. Relative arrangement of TTF and TCNQ molecules. Arrows represent the amplitudes of the main modulation waves enlarged by a factor 100. The TCNQ modulation has a component along the molecular normal, while the TTF modulation represents a slip along the long molecular axis.

X-RAY STANDING WAVE MEASUREMENTS AT BRAGG ANGLES CLOSE TO 90 DEGREES. K.-G. Huang, J. Zegenhagen, W.M. Gibson (SUNY/Albany) and J.C. Phillips (SUNY/Buffalo).

The X-ray standing wave (XSW) technique is a sensitive probe for investigating the structure of the surface and interface region of perfect single crystal substrates (1). With an (hkl) reflection the (hkl) Fourier component of the distribution function of atoms under consideration is determined. XSW data are taken scanning in angle within the range of total Bragg reflection. The reflection curves become very narrow for high (hkl) indices. However, for Bragg reflections close to 90 degrees the rocking curve width $\Delta\theta$ increases drastically to $(\Delta\theta \sim \sin^{-1}(2\theta))$. We performed XSW measurements for NiS_2 MBE produced epitaxial layers on Si(555), with Bragg angles up to 89.4 degrees. Higher order Fourier components could be determined. The wide rocking curves (32 sec of arc in our case) may allow use of less perfect substrates where commonly XSW measurements are not possible.

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X-RAY REFLECTIVITY AND INTERFACIAL ROUGHNESS. Y.H. Kao (SUNY/Stony Brook).

We have recently carried out extensive studies of X-ray reflectivity and developed a new method for determining the interfacial roughness between different materials in semiconductor heterostructures. By using grazing angle X-ray incident on semiconductor heterostructures, we have found pronounced oscillations in the reflectivity. These oscillations are later identified as the analogue of the Newton's ring effect in the X-ray wavelengths. The angular dependence of these oscillations is related to the thickness of the epilayer and the interfacial roughness. By a comparison between the experimental data and a theoretical model based on the Fresnel equations modified to include some roughness parameters, we were able to determine for the first time the interfacial roughness of a sub-surface interface between InAs and GaAs. Also, the thickness of the epilayer was accurately determined. These results have been submitted for publication.

SMALL ANGLE X-RAY SCATTERING OF POLYSTYRENE IONOMERS. Ben Chu, D.-Q. Wu, C. Wu (SUNY/Stony Brook), W.J. MacKnight, C.W. Lantman (U. of Massachusetts), J.C. Phillips and A. LeGrand (Brookhaven National Laboratory and SUNY/Buffalo), R.D. Lundberg (Exxon).

Small angle X-ray scattering (SAXS) studies using a new modified Kratky block collimation system have been made on polystyrene ionomers. The sulfonated polystyrene ($M_w = 1.15 \times 10^5$) samples include both narrow and broad molecular weight distributions ($M_w/M_n = 1.04, 2.66$) in acid form as well as sodium and zinc salts. The mole % sulfur varies from 1.3 to 4.5 with the exception of sodium salt form to 7.5. We were able to achieve a q range between 0.1 and 7.5 nm^{-1} where $q = (4\pi/\lambda)\sin(\theta/\lambda)$ with $\lambda = 0.154 \text{ nm}$ and θ being the scattering angle.

We have been able to measure the details of the static structure factor including the temperature effects from 27°C to 250°C. The nature of the ion clusters, including variations in cation form, polydispersity and ion content give information on inter- and intramolecular interference models.

MULTI-TEMPERATURE EXAFS SPECTROSCOPY OF SIX COORDINATE, HIGH SPIN MESO-TETRAPHENYLPORPHINATO-BIS-TETRAHYDROFURAN IRON(II). T. F. McNulty, J. C. Phillips, P. Coppens (SUNY/Buffalo).

The high spin, six coordinate iron porphyrin meso-tetraphenyl-porphinato-bis-tetrahydrofuran iron(II) (FeTTP(THF)₂), has been studied using EXAFS spectroscopy. Our low-temperature crystallographic analysis, done at a conventional source, showed a large contraction of the axial Fe-O bond between room- and liquid-nitrogen temperatures. Magnetic measurements showed anomalies in the paramagnetism below the latter temperature. In order to investigate if a further contraction below liquid-nitrogen can explain the magnetic observations a series of EXAFS experiments were conducted at various temperatures down to 20K. The results convincingly show that no further contraction occurs. The observed increase in magnetic moment remains unexplained.

PROTEIN FOLDING OBSERVED BY TIME-RESOLVED SYNCHROTRON X-RAY SCATTERING - A FEASIBILITY STUDY.
James C. Phillips (SUNY/Buffalo).

The ability to calculate the 3D structure of proteins from knowledge of their sequence (or their gene sequence) would be a major advance in biology and biotechnology. The database for such calculations can be enhanced by knowledge of intermediate structures from time-resolved measurements of proteins folding and unfolding in solution. This project seeks to test the feasibility of using a powerful synchrotron radiation source, combined with T-jump and time-resolved X-ray scattering techniques to investigate pathways of protein folding. We have used the SUNY X21 beamline, SAXS bench and time-resolved data acquisition system for initial studies in this area. A temperature jump apparatus was constructed to study thermally induced folding and unfolding. Scattering of solutions of myoglobin in the angular range $2\theta = 1-50$ mrad was measured during temperature jumps between 26 and 76°C. T-raise data show clear signs of structural changes (Figure 1), however, the T-drop experiments show minimal changes. Moreover, the T-raise changes are reproducible only qualitatively, not quantitatively. A tentative interpretation of the observations is as follows: (1) heating to 55°C, no big structural change (2) by 65°C partial unfolding with increased radius of gyration followed by (3) mostly unfolded followed by (4) irreversible aggregation.

Figure 1. Time-resolved Measurement of x-ray Scattering of a Solution of Sperm Whale Myoglobin as the Temperature is Raised.

PEROVSKITE. C.T. Prewitt (Geophysical Lab. Washington, DC) and D.J. Weidner (SUNY/Stony Brook).

The perovskite crystal structure is of interest because its derivatives constitute the high T_c superconductors that have been the focus of widespread inquiry in the past few months. $(\text{Mg,Fe})\text{SiO}_3$ perovskite is thought to be the most abundant mineral in the earth, comprising the bulk of the lower mantle below 670 Km. The orthorhombic MgSiO_3 perovskite structure has two crystallographic sites, one normally occupied by Si in octahedral coordination and the other occupied by eight-coordinated Mg. A recent EXAFS and XANES study at SSRL on $(\text{Mg,Fe})\text{SiO}_3$ synthesized in a diamond-anvil cell indicated disorder between these two sites with Fe on the octahedral site and, presumably, Si on the eightfold position (1). This is an unexpected result that has important implications for the phase equilibria of the lower mantle and for silicate crystal chemistry. One problem with these experiments is that only a very small quantity of material can be made in the diamond cell, i.e., a disk-shaped polycrystalline sample about 80-100 microns in diameter and 20 microns thick. Our intention in this experiment was to obtain a powder diffraction pattern and to analyze the cation distribution through profile fitting of the pattern by the Rietveld technique. Figure 1 shows the observed pattern for $(\text{Mg}_{0.9}, \text{Fe}_{0.1})\text{SiO}_3$. However, because of the very high background, we have been unable to verify whether disorder is present in the sample. Further experiments will have to be made after much more effort has been made to reduce the background through the addition of slits and collimators to the diffractometer system on the beamline. Also, the X-ray wavelength used, 1.41 Å may be causing fluorescence in the sample.

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Figure 1. Powder diffraction pattern of 10% Fe perovskite, 8.8 keV photons.

THERMAL DIFFUSE SCATTERING IN KMgF_3 AT ROOM TEMPERATURE AND ELEVATED TEMPERATURES. D.J Weidner, Amir Yeganeh-Haeri (SUNY/Stony Brook), D. Swanson, (DuPont), and C.T. Prewitt, (Geophysical Lab., Washington, DC).

Previous attempts to isolate the thermal diffuse scattering contribution to the scattered X-ray intensities have proven unsuccessful. This experiment was designed to optimize the possibilities of observing such a signal by observing the X-ray scattering at elevated temperatures and at a higher scattering angle.

A 300 micron single crystal which was spherical in shape was used in the experiments. X-ray intensities were collected at the (0 3 3) Bragg reflection. Intensities were measured along 3 perpendicular directions extending 0.08 reciprocal lattice vectors away from the Bragg spot at intervals of 0.01. The TDS intensities of these three lines should be proportional to: $1/(q^2C)$, where q is the distance from the Bragg position in reciprocal space and C is the elastic modulus $(C_{11} + C_{12} + 2C_{44})/2$, C_{44} , or $(C_{11} - C_{12})/2$ depending on which line.

The slope of a straight line for I vs. $1/(q^2C)$ should be proportional to $1/C$. The data can thus be evaluated as to whether or not the ratios of slopes for two such lines agrees with the known ratios of elastic moduli.

The room temperature data are not consistent with the intensities observed in this region being of TDS origin. The intensities and slopes for the line parallel to (0 1 1) (which is the two theta-omega direction and corresponds to the longitudinal acoustic direction of the TDS) are both quite low. The two perpendicular lines by comparison yield slopes that are an order of magnitude too large. Thus, while the shape has the correct sign, the shape of the diffuse scattering intensity contour is too much like a pancake relative to that expected from TDS. These results were reproduced in two data sets and qualitatively in agreement with the previous experience.

The high temperature (600 C) results are much more encouraging. The slopes are consistent with those expected from TDS with about a factor of two uncertainty. This uncertainty is a reflection of the reproducibility of the results.

We conclude that we have detected diffuse scattering that is dominated by TDS. However, it is still not usable to determine the single crystal elastic properties or their variation with pressure or temperature. Counting time can be extended to give a better statistical evaluation of the high temperature data. However, longer counting times would not qualitatively improve the room temperature data. The use of TDS as a means of exploring elastic properties using synchrotron radiation and small samples probably awaits higher resolution of the energy of the detected X-ray (perhaps 0.01 eV).

THE FIRST GAMMA-RAY BEAM AT LEGS

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The first gamma-ray beams from the Laser-Electron-Gamma-Source (LEGS) were produced on Thursday, May 21, 1987 during a three week period of initial tests. Gammas were also successfully tagged in this test run. UV light at 351 nm from an Ar-ion laser was backscattered from 2.5 GeV electrons circulating in the X-ray ring to produce gamma-rays up to 300 MeV. The spectrum of gamma-rays, observed by a 10 by 14 inch NaI(Tl) detector, is shown at the top of the figure. The lower part of the figure is the spectrum of gamma-rays in coincidence with electrons detected at an intermediate point in the partially completed tagging spectrometer. The measured rate of the gamma-ray beam, normalized to the stored beam current and laser power, was 35 per second-MeV-mA-Watt. Both the shape of the spectrum and the observed rate are in excellent agreement with calculated predictions. At the full ring current of 300 mA and with 3 watts of UV power, the backscattered gamma-ray beam rate will be 107 per second.

These tests followed a shutdown period in the spring during which a part of the LEGS equipment was installed in the X-ray ring tunnel. The principal items installed were the modified dipole vacuum chamber, one of the magnets for the tagging spectrometer, and a CO₂ laser in the center of the injection straight section for measuring the energy of the stored beam. The Ar-ion laser was installed in the LEGS hutch prior to the beginning of the shutdown. During the test period the computer controlled aiming system for the laser demonstrated its capabilities both in finding the alignment of the laser beam with the electron beam in the injection straight section and in maintaining this alignment to produce a stable gamma-ray beam. The measured positioning accuracy of the laser optical system is 10 micrometers and 10 microradians. Definitive tests of the operation of the CO₂ laser system were not possible because of the poor vacuum in the injection straight section.

The tagging spectrometer for LEGS consists of four dipole magnets, the first of which is the ring dipole X1BM1. The second dipole is a septum magnet with a gradient field which will operate with a field of 2 T at 3 cm from the stored beam. This magnet has been carefully designed to minimize the leakage field at the stored beam. It is made of Hiperco-50, an alloy of iron and cobalt that has high permeability at high fields (40,000 at 1.9 T), and the current septum has been located outside the magnetic gap along the front face of the magnet in such a way as to cancel the gradient of the leakage field at the position of the stored beam. Three sets of trim coils wound on the front face of the magnet are used to further minimize the leakage field. This magnet was thoroughly tested before installation in the X-ray ring, and can produce fields in the working gap up to 2.2 T with leakage fields less than 2.5×10^{-5} T at the stored beam. During the test period with beam in the ring, repeatedly turning this magnet on and off produced no change in the orbit at 2.5 GeV as determined by the PUE's.

Spectrum of gamma-rays from Compton backscattering with no tagging, at top, and with energy defining electron tag at 300 MeV, at bottom.

THE CRYSTAL STRUCTURE OF AN AS-SYNTHESISED $\text{AlPO}_4\text{-16}$

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$\text{AlPO}_4\text{-16}$ is a member of the novel aluminophosphate-based families of molecular sieves which are an important new class of catalyst and adsorbent materials. Data were collected from a flat plate sample and indexed on a cubic cell with $a_0 = 13.384\text{\AA}$, the space group was determined to be F23. The framework topology was determined using a modelling technique applicable to tetrahedral framework structures. The data were refined using the DLS-Rietveld program of Ch. Baerlocher. The framework topology consists of double four rings interconnected by single tetrahedra in an arrangement similar to that reported for the mineral Zunyite but with no tetrahedral vacancies. The organic template (quinuclidine) is disordered and has been successfully modelled in the center of the large cavity. The final positional parameters and the result of the Rietveld refinement are shown below, the differences in the tails of the peaks are caused by particle size broadening. The assistance of Ch. Baerlocher and G. Harvey at ETH, Zürich, Switzerland during the final stages of this structure determination is gratefully acknowledged.

Atom	x	y	z	mult.	Atom	x	y	z	mult.
Al1	0.11547	0.11547	0.11547	0.3333	P1	-.11527	0.11527	0.11527	0.3333
Al2	0.75	0.25	0.25	0.0833	P2	0.25	0.25	0.25	0.0833
O1	-.01384	0.13025	0.14632	1.0	O2	0.18913	0.18913	0.18913	0.3333
O3	-.17591	0.17591	0.17591	0.3333	N1	0.0560	0.4329	0.0424	1.0
C1	0.0056	0.3916	-.0462	1.0	C2	-.0601	0.4680	-.0973	1.0
C3	0.1159	0.5193	0.0103	1.0	C4	0.0529	0.5988	-.0393	1.0
C5	-.0214	0.4689	0.1118	1.0	C6	-.0878	0.5472	0.0646	1.0
C7	-.0552	0.5662	-.0418	1.0	H7	-.0978	0.6173	-.0741	1.0
H11	0.0566	0.3668	-.0939	1.0	H12	-.0351	0.3331	-.0261	1.0
H21	-.0382	0.4774	-.1673	1.0	H22	-.1300	0.4437	-.0995	1.0
H31	0.1506	0.5481	0.0691	1.0	H32	0.1686	0.4965	-.0364	1.0
H41	0.0592	0.6627	-.0025	1.0	H42	0.0772	0.6110	-.1081	1.0
H51	-.0626	0.4116	0.1344	1.0	H52	0.0112	0.4970	0.1722	1.0
H61	-.1583	0.5246	0.0658	1.0	H62	-.0845	0.6099	0.1036	1.0

¹Work was supported by the Division of Materials Sciences, U. S. Department of Energy, under contract DE-AC02-76CH00016.

APPLICATION OF HIGH RESOLUTION SYNCHROTRON POWDER X-RAY
DIFFRACTION TO THE STRUCTURAL INVESTIGATION OF A
NEW NON LINEAR OPTICAL MATERIAL.

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Ammonium titanyl phosphate (NTP) is a new non-linear optical material which shows considerable promise in waveguiding, electro-optic and second harmonic applications. The structure of NTP is analogous to the potassium derivative (KTP) which is the premier material used for second harmonic generation of the 1.06 μ YAG laser.

Our structural studies have shown that by using ion exchange or thermal treatments the structure and non-linear optical properties of NTP can be altered considerably. However these procedures usually result in a loss of the single crystal integrity. Consequently powder methods are required for any structural investigations.

The aim of our research in this area is to be able to manipulate the structure, and hence the non-linear optical properties by using simple chemical methods, such as ion-exchange or thermal treatments. To this end a sample was prepared, designated NOTP, in which half of the ammonium had been calcined from the structure, and this had then been hydrated. This material exhibited a second harmonic signal equivalent to KTP or NTP and is the subject of this investigation.

In the early stages of data reduction it was clear that additional peaks, which could not be indexed using the orthorhombic cell of NOTP, were present in the powder pattern. Consequently, these were excluded from the refinement until the least squares had converged and all of the extra-framework material had been located by Fourier techniques. The final results are given in table 1. Then the calculated powder profile for NOTP was subtracted from the raw data and the structure of the impurity phase refined using this difference data. The impurity was found to be anatase, although the lines are substantially broadened. This phase results from partial collapse of the titanium phosphate framework.

Table 1. Final Atomic Positions for NOTP.

Space Group Pna2 ₁ (Int. Tables I No.33)						
Atom	site	x/a	y/b	z/x	B(Å ²)	occ.
Ti(1)	4a	0.3716(2)	0.499(1)	0.000	1.29(6)	1.0
Ti(2)	4a	0.2488(7)	0.263(1)	0.251(1)	1.29	1.0
P(1)	4a	0.4976(9)	0.339(1)	0.255(2)	1.12(8)	1.0
P(2)	4a	0.1830(4)	0.506(2)	0.509(1)	1.12	1.0
O(1)	4a	0.490(2)	0.486(3)	0.145(1)	0.86(8)	1.0
O(2)	4a	0.519(2)	0.460(3)	0.380(1)	0.86	1.0
O(3)	4a	0.400(1)	0.181(3)	0.290(2)	0.86	1.0
O(4)	4a	0.594(1)	0.213(2)	0.246(1)	0.86	1.0
O(5)	4a	0.116(1)	0.310(3)	0.542(2)	0.86	1.0
O(6)	4a	0.116(1)	0.682(3)	0.479(2)	0.86	1.0
O(7)	4a	0.247(2)	0.560(3)	0.624(2)	0.86	1.0
O(8)	4a	0.260(2)	0.458(3)	0.385(2)	0.86	1.0
O(9)	4a	0.219(1)	0.034(3)	0.650(1)	0.86	1.0
O(10)	4a	0.231(1)	0.050(3)	0.391(2)	0.86	1.0
O(11)	4a	0.385(1)	0.786(2)	0.327(1)	1.04(9)	1.0
N(1)	4a	0.394(1)	0.193(2)	0.576(2)	1.04	1.0
a		12.9154(1)Å	R _I	-	6.0%	
b		6.4946(1)Å	R _{wpr}	-	19.5%	
c		10.5886(1)Å	R _{exp}	-	14.7%	

* Work supported by the Division of Materials Sciences, U.S. Dept. of Energy, under contract DE-AC02-76CH00016

DETERMINATION OF THE STRUCTURE OF CdS/CdSe CLUSTERS
IN ZEOLITE-Y BY HIGH RESOLUTION POWDER SYNCHROTRON X-RAY DIFFRACTION

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Small metal and semiconductor particles, having hybrid molecular and bulk properties, represent a new class of materials and are presently under intensive investigation. Many approaches exist for preparing these small clusters. However in almost all of the methods used to date the size of the cluster is not well defined. A new approach, which we have adopted, is to prepare the desired cluster inside an open framework host material. The host chosen for these studies was zeolite-Y which has the largest void volume of any zeolite.

The optical properties of zeolite-Y loaded with differing concentrations of CdS and CdSe have been monitored by diffuse reflectance vis/U.V. spectroscopy¹. In order to understand the unusual optical properties displayed by these materials a detailed knowledge of their structure is essential. Large single crystals of zeolite-Y are not available, so powder methods have dominated in the structural investigation of this aluminosilicate. The high resolution and intensity available at a synchrotron source are ideal for collecting data from these large unit cell, weakly scattering materials.

The moisture sensitive samples were loaded into the aluminum containers and sealed with thin beryllium foil. Exposure to the air causes migration of the semiconductor to the zeolite surface. Beryllium forms a protective layer which is non-absorbing, and the small number of diffraction peaks are easily excluded from the data.

Figure 1 shows the observed, calculated and difference profiles for one of the samples studied (CdSe in zeolite-Y). It is quite apparent that the pattern calculated from the refined model is in excellent agreement with the data.

Figure 1. Observed (dots), calculated (solid line) and difference (sub-plot) profiles for CdSe in zeolite-Y.

In all cases the framework is essentially unchanged from that of the parent zeolite-Y and the mean T-O bond distances are in excellent agreement with that calculated from the Si/Al ratio. Cadmium occupies two sites, one in the sodalite six-ring, the other in the supercage twelve-ring, while the sodium remaining after ion exchange is in the most favorable position, the six-ring window of the framework. The coordination complement of the cadmium is made up from framework oxygen, oxygen of hydroxide ions left after dehydration, and S or Se.

^{*} Work supported by the Division of Materials Sciences, U.S. Dept. of Energy, under contract DE-AC02-76CH00016.

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ATOMIC STRUCTURE OF QUASICRYSTALS (X7-A)

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Objective and Approach

Extensive theoretical and experimental studies have been carried out on the structure of quasicrystals, however, many fundamental questions remain unsolved. It is still actively debated whether the icosahedral solid is truly a quasicrystal described by a 3-dimensional Penrose tiling (3-DPT) structure, or merely an orientationally ordered glass. Furthermore the actual atomic structure has not been determined. To address both of these problems we carried out differential anomalous-x-ray-scattering measurements to obtain the total and differential atomic pair distribution functions (PDF's), and compared the results with structural models.

Results

The scattering intensities from the icosahedral (I) phase of $\text{Al}_{5.5}\text{Li}_{3.3}\text{Cu}$ were found to compare well with to the one calculated for a 3-DPT structure with Al and Cu atoms at the vertices and edge centers [1]. The total PDF of the I-phase and that of the Frank-Kasper (FK) phase of the same composition are very similar up to 20 Å as shown in Fig. 1 [2], supporting the model by Henley and Elser, and small differences between these PDF's suggest that the I phase is not made of packed icosahedral clusters as the icosahedral glass (IG) model assumes. The uranium differential distribution function (DDF), which is the atomic distribution function with uranium atoms at origin, of icosahedral $\text{Pd}_{58.8}\text{U}_{20.6}\text{Si}_{20.6}$ was determined by the differential anomalous-x-ray-scattering (DAS) [3]. The DDF agrees very well with the PDF calculated for a 3-DPT structure with the quasilattice constant of 5.14 Å and with U atoms placed at each vertex, in the range of 12 to 40 Å, as shown in Fig. 2 [4]. Also the physical density of the 3-DPT model was in very good agreement with the uranium density in the sample. The IG models (C and D in Fig. 2) show less satisfactory agreement. The DAS measurement of I-phase $\text{Al}_{78}\text{Ru}_{55}\text{Mn}_{17}$ shows that Ru atoms occupy the vertex positions of a quasicrystalline sublattice [5]. These results demonstrate that some icosahedral solids are indeed best described as decorated 3-DPT quasicrystals, and gave further insights regarding the mechanism of their stability.

Acknowledgments

The authors are grateful to the members of the PRT at X13-A (now X7-A), particularly to D. E. Cox. This work has been supported by the National Science Foundation through the Grants DMR83-18816, DMR86-17950, DMR85-19059, DMR84-02642, and DMR82-16718.

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Fig. 1. Atomic pair distribution function of icosahedral and Frank-Kasper phases of $\text{Al}_{5.5}\text{Li}_{3.3}\text{Cu}$ [2].

Fig. 2. Uranium DDF of I-Pd_{58.8}U_{20.6}Si_{20.6}(A), PDF's of 3-DPT(B), and icosahedral glass models (C and D) [4].

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ZSM-5 and ZSM-11 belong to a family of shape-selective catalysts which have important industrial applications. Their structures consist of open frameworks of essentially rigid SiO_4 tetrahedra characterized by ten-membered ring apertures which can admit certain types of hydrocarbon molecules. As shown in Fig. 1 there are substantial differences in the magic angle spinning NMR spectra from ZSM-11 at 25°C and 100°C indicative of some kind of symmetry change. High resolution synchrotron x-ray powder data have been collected at these temperatures from a 1mm diameter capillary specimen mounted in a furnace. A Ge(111) monochromator and a LiF(400) analyzer crystal were used, with $\lambda=1.315\text{\AA}$. The use of a capillary specimen greatly reduces preferred orientation effects, but does not lead to any loss of resolution in the diffraction pattern when the crystal-analyzer technique is used. Although no change in crystallographic symmetry can be detected at 25°C, preliminary analysis indicates some significant changes in the environment of the Si atoms which might correspond to local symmetry changes. Full structure refinements, involving 76 structural parameters, are nearing completion.

Temperature dependence data have also been collected from a 1mm capillary sample of ZSM-5, which is known to undergo a transition from monoclinic to orthorhombic symmetry at about 100°C, or as a function of absorbed hydrocarbon content. Some representative scans showing the splitting of the orthorhombic (133) peak are shown in Fig. 2. There is an appreciable range of coexistence of the two phases, and a build-up of some diffuse scattering between the monoclinic (133) and (133) peaks preceding the appearance of the orthorhombic phase. A structure refinement of the latter at 150°C is in progress.

Fig. 1. ^{29}Si MAS-NMR Spectra from ZSM-11.

Fig. 2. Evolution of ZSM-5 Monoclinic (133) and (133) Peaks as a Function of Temperature.

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† Work supported by US DOE contract No. DE-AC02-76CH00016.

STATIC COMPRESSION OF H₂O-Ice TO 128 GPa (1.28 MBAR)

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The high-pressure behavior of H₂O is of fundamental importance in both condensed matter and planetary physics.^{1,2} The hydrogen bonding in this system gives rise to a variety of phases at low pressures and temperatures (i.e., < 2 GPa and < 300 K), including the recently discovered high-density amorphous phases.³ Structural and equation of state and spectroscopic studies have been carried out in the 30-50 GPa range on the dense ices (ice VII and VIII), but no experimental data are available on the properties of solid H₂O in the megabar pressure range (>100 GPa) where a variety of stable phases, including the metallic form, have been proposed. Information on the properties of H₂O at these pressures has been limited to the results of shock-wave experiments, which probe the *fluid* phase at high pressures and temperatures, and to theoretical statistical electron calculations. In the present study, we have compressed ice in a diamond-anvil cell to 128 GPa and measured the molar volume as a function of pressure by synchrotron x-ray diffraction techniques. The room-temperature equation of state is shown in Figure 1. The diffraction data are consistent with the body-centered cubic oxygen sublattice of ice VII persisting to the highest pressures of our measurements. The measured equation of state indicates that ice is less compressible at very high pressures than is suggested by recent experiments in the 30-50 GPa range, but more compressible than statistical electron and recent pair-potential models predict.

Fig. 1 Pressure-volume data and calculated room-temperature equation of state for H₂O-ice.

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Work supported by the Carnegie Institution of Washington, the National Science Foundation (grants EAR-8314064, EAR-8418706, EAR-8419982), and by NASA (contract NAGW214). †Work supported by The Division of Materials Sciences, U.S. Department of Energy, contract DE-AC02-76CH00016.

EQUATION OF STATE OF NEON TO 110 GPa

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The properties of condensed gases at ultrahigh pressures continue to attract much experimental and theoretical attention as these systems provide critical tests of theoretical models of bonding in solids¹. Solid neon was compressed to 110 GPa (1.1 Mbar) in a diamond-anvil cell to determine its structure and pressure-volume equation of state. Energy-dispersive and micro-collimation methods were employed to obtain diffraction data at ultrahigh pressure. The maximum compression, corresponding to a relative volume $V/V_0 = 0.28$ at 110 GPa is among the largest measured by x-ray diffraction techniques. Neon remains an insulator with the *fcc* structure over this pressure interval. The measured P-V isotherm at high pressure is poorly described by the available pair potentials for neon (Fig. 1) but is in excellent agreement with the results of electronic structure calculations. The determination of an accurate Ne-Ne pair potential has been the subject of much controversy in recent theoretical studies of rare-gas solids, and there is no consensus on the role of many-body forces in solid neon. The present data provide important constraints on the role of pair and many-body forces in this material at high compressions.

Fig. 1 Pressure-volume data and calculated equations of state for solid neon. The solid and dashed lines are fits of a Birch-Murnaghan equation of state to the experimental data. The dash-dot line was calculated from the HFD-C2 pair potential of Ref. 3, with the P_{zz} and P_{TH} contributions calculated from quasi-harmonic lattice dynamics (see Ref. 1).

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$\text{Ca}_{0.75}\text{Nb}_3\text{O}_6$: A NOVEL METAL OXIDE CONTAINING NIOBIUM-NIOBIUM BONDS. CHARACTERIZATION AND STRUCTURE REFINEMENT FROM SYNCHROTRON POWDER X-RAY DATA

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High resolution synchrotron x-ray powder data collected at beam-line X13A have been used to refine the structure of a novel mixed metal oxide $\text{Ca}_{0.75}\text{Nb}_3\text{O}_6$. The composition of the latter was determined by analytical electron microscopy. The unit cell is orthorhombic, space group Immm with lattice parameters $a=7.113\text{\AA}$, $b=10.286\text{\AA}$, $c=6.563\text{\AA}$. The atomic coordinates are listed in Table I, selected bond angles and distances in Table II, and views of the structure in Figs. 1 and 2. An interesting feature of the structure is the presence of an extremely short Nb-Nb bond distance of $2.58\text{\AA}$ within an Nb_2O_8 unit.

Table I. Profile and Structural Parameters from the Rietveld Analysis of the Synchrotron Data

Profile Parameters					
half-width parameters (0.01°)					
Gaussian: $U = 166$ (8), $V = -66$ (5), $W = 8.9$ (6)					
Lorentzian: $X = 4.3$ (1), $Y = 0$					
zero point (0.01°): -0.87 (3)					
cell constants: $a = 7.112$ (7) $\text{\AA}$, $b = 10.285$ (10) $\text{\AA}$, $c = 6.562$ (6) $\text{\AA}$					
Structural Parameters					
overall isotropic temperature factor: 0.20 (7) $\text{\AA}^2$					
Fractional Atomic Coordinates in Immm (No. 71)					
atom	sym position	x	y	z	atoms/unit cell
Nb(1)	4j	0.0000	0.5000	0.3036 (5)	4
Nb(2)	8n	0.2278 (3)	0.2808 (2)	0.5000	8
Ca	4i	0.5000	0.5000	0.238 (2)	3.03 (6)
O(1)	4g	0.5000	0.668 (2)	0.5000	4
O(2)	4h	0.5000	0.678 (2)	0.0000	4
O(3)	16o	0.820 (2)	0.366 (1)	0.232 (1)	16

$$R_{\text{nuc}}^a = 12.5\%, R_{\text{prof}} = 15.9\%, R_{\text{wprof}} = 19.5\%, R_{\text{expected}} = 6.1\%$$

^a R_{nuc} is the reliability factor based on approximate integrated intensities.¹⁵

Table II. Bond Angles ($^\circ$) and Distances ($\text{\AA}$) for CaNb_3O_6

Nb(1)-Nb(1)	2.578 (7)	Nb(2)-O(2)	1.930 (20)
Nb(1)-Nb(2)	3.061 (4) ($\times 4$)	Nb(2)-O(3)	1.992 (20) ($\times 2$)
Nb(2)-Nb(2)	3.241 (6)	Nb(2)-O(3)	2.240 (20) ($\times 2$)
Nb(2)-Nb(2)	3.357 (6) ($\times 2$)	Ca-O(1)	2.432 (24) ($\times 2$)
Nb(1)-O(3)	1.941 (20) ($\times 4$)	Ca-O(2)	2.415 (24) ($\times 2$)
Nb(2)-O(1)	2.008 (20)	Ca-O(3)	2.666 (26) ($\times 4$)
Nb(1)-Nb(2)-Nb(1)	49.8	O(3)-Nb(1)-O(3)	152.0
Nb(2)-Nb(1)-Nb(2)	63.9	Nb(2)-O(2)-Nb(2)	114.2
Nb(2)-Nb(1)-Nb(2)	94.9	Nb(2)-O(1)-Nb(2)	149.3
Nb(1)-O(3)-Nb(2)	102.2

Figure 1. Structure of $\text{Ca}_{0.75}\text{Nb}_3\text{O}_6$ viewed down z (Ca, hatched circles; Nb, small circles; O, large open circles).

Figure 2. Structure of $\text{Ca}_{0.75}\text{Nb}_3\text{O}_6$ viewed down x

* Work supported by U.S. Department of Energy contract No. DE-AC02-76CH00016.

STATIC COMPRESSION OF CORUNDUM TO 170 GPa (1.70 MBAR)

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Compression data for ruby ($\text{Al}_2\text{O}_3 \approx 0.05\% \text{ Cr}^{3+}$) have been obtained by energy-dispersive scattering in a diamond-anvil cell to 170 GPa (1.7 Mbar). Diffraction was observed from ruby powder ($\leq 5 \mu\text{m}$) included with the sample for calibration of the pressure in a static compression experiment at room temperature. Information on the structural behaviour of ruby to such pressures is useful because of its frequent usage as a secondary pressure calibrant in static compression studies and recent theoretical predictions of an instability in corundum at ultra high pressures. Results from the present work indicate that, within the comparatively large uncertainty in pressure due to the weakening and broadening of R_1 - R_2 lines under nonhydrostatic compression, ruby does not undergo any reconstructive structural transition to at least 170 GPa. The large stress gradients that exist under nonhydrostatic compression also rule out the possibility that corundum is elastically unstable up to the pressures of this study. The unit-cell volumes are plotted as a function of pressure in Figure 1. At the highest pressure, the volume measured is consistent with both an extrapolated equation of state from ultrasonic measurements¹ and one derived from single-crystal studies to 5 GPa [2] with $K_0 \approx 254 \text{ GPa}$, $K'_0 \approx 4.3$. There is also excellent agreement with a first-principles calculation of the equation of state using the potential-induced breathing model³. The c/a ratio obtained from refinements of the strongest lines in the EDS spectrum (Fig. 2) remains constant throughout the pressure range at 2.73 ± 0.05 and equals the value at zero pressure. A more sensitive indication of the onset of a possible structural distortion at high pressure, however, could be obtained by high-pressure vibrational spectroscopy. This work demonstrates that P-V studies can be carried out on low-Z materials in the megabar pressure range ($>100 \text{ GPa}$).

Fig. 1 Pressure-volume data for $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ to 170 GPa.

Fig. 2 Volume dependence of c/a for $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$.

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PRESSURE-INDUCED STRUCTURAL TRANSITIONS IN CONDENSED GASES

A.P. Jephcoat, H.-k. Mao, L.W. Finger, R.J. Hemley, C.-s. Zha (Geophysical Laboratory, Washington, D. C.), and D.E. Cox[†] (BNL).

The properties of condensed gases as a function of pressure are of fundamental importance in condensed-matter physics. In particular, the relative stability of the crystal structures of the rare-gas solids has been the focus of many theoretical models¹, as has the insulator-to-metal transition in atomic and molecular systems². We report results of energy-dispersive x-ray diffraction studies at high pressure on solid xenon and solid nitrogen performed with a finely-collimated, white x-ray beam at beamline X13A. Xenon was compressed to 137 GPa (the highest pressure to be obtained with a soft sample) and nitrogen to ~65 GPa. A synchrotron source was indispensable for both experiments in order to compensate for the effects of very small scattering volumes (Xe sample thickness at 137 GPa $\leq 10\mu\text{m}$) and the low intrinsic scattering cross section of N_2 .

Two structural transitions were observed in xenon (Fig. 1). The fcc phase is unstable above 14 GPa and transforms to a phase that appears to be a close-packed polytype similar in structure to the rare-earth metals. Above ~75 GPa a transformation to the hcp structure takes place. The existence of the intermediate phase between fcc and hcp is important because structures with mixed cubic and hexagonal packing have not been considered in theoretical models of rare-gas solids.

The structural transitions observed in solid nitrogen are shown in Figure 2. The initial changes in the diffraction pattern to 16.4 GPa result from the breakup of large crystallites in the sample chamber. The structural transitions at higher pressures can be correlated with branching of the low-frequency vibron in molecular nitrogen observed by spectroscopic methods.

Fig. 1 Energy-dispersive x-ray diffraction spectra of solid xenon to 137 GPa.

Fig. 2 Energy-dispersive x-ray diffraction spectra of solid nitrogen to ~65 GPa.

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SINGLE-CRYSTAL X-RAY DIFFRACTION OF SOLID HYDROGEN AND DEUTERIUM

A.P. Jephcoat, H-k. Mao, R.J. Hemley, L.W. Finger, R.M. Hazen, C-s. Zha (Geophysical Laboratory, Washington, D. C.), and D.E Cox[†] (BNL).

The equations of state (EOS) of solidified $n\text{-H}_2$ and $n\text{-D}_2$ have been determined directly by x-ray scattering methods to pressures of 26 GPa and 14 GPa, respectively (Figs. 1 and 2). A combination of single-crystal, diamond-anvil cell techniques and energy-dispersive x-ray diffraction methods resulted in the successful determination of unit-cell volume at these high pressures and room temperature. Initial work at 5.4 GPa, just above the room-temperature freezing pressure, was performed with a conventional sealed Mo-K α source¹ and a large sample volume. It was found that solid H_2 adopts the hexagonal close-packed structure, $P6_3/mmc$, $Z=2$. In order to extend the P-V measurements to higher pressures, significantly smaller sample volumes were required with a consequent reduction in scattering intensity. The experiment was also made more difficult by the breakup and re-orientation of the hydrogen single crystals on compression. Such problems were again minimized by use of finely-collimated, intense x-ray beam.

These data provide, for the first time, unambiguous constraint on the room-temperature equations of state of these molecular solids—previous determinations of the hydrogen EOS^{2,3} were in notable disagreement with each other. A room-temperature EOS was derived from the data of Ref. 3 by Hemmes *et al.*⁴. The new data plot with intermediate volumes at all pressures (Fig. 1).

Fig. 1 Pressure-volume data for solid $n\text{-H}_2$ to 26.6 GPa. Fig. 2 Pressure-volume data for solid $n\text{-D}_2$ to 14.0 GPa.

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AB INITIO STRUCTURE DETERMINATION FROM POWDER DIFFRACTION DATA

Lynne B. McCusker (Oxford University, U.K.)

Knowledge of the aluminosilicate framework structure of zeolitic materials is essential to the understanding of their unique chemical and catalytic properties. Unfortunately, most new synthetic zeolites are only available in polycrystalline form, so single-crystal diffraction techniques cannot be applied. Since their structures are so important, a number of ingenious indirect methods have been developed over the years, but interpretation of the data is heavily dependent upon experience and intuition.

With the advent of synchrotron radiation, very high resolution x-ray powder diffraction has become possible and a crystallographic approach to the problem more feasible. The higher resolution allows a much less ambiguous decomposition of the powder diffraction pattern than was previously possible. Although overlapping reflections are not eliminated, they are minimized. Once reliable integrated intensity values have been calculated, a single-crystal structure determination procedure can be followed.

In order to investigate the feasibility of this approach to zeolite structure solution, data on three samples (one with a known, one with a proposed and one with an unknown structure) were collected on beam line X13A at the NSLS. A series of computer programs for processing the data had already been assembled, modified and tested for this purpose using data from the SRS facility in Daresbury, U.K.

The highlight of this investigation has to be the solving of the previously unknown structure of Sigma-2 directly from the powder diffraction data. Sigma-2 is a new clathrasil phase and closely related to the zeolite family of materials. Data were collected with: $\lambda = 1.5468 \text{ \AA}$, $0.01^\circ 2\theta$ steps, 4-10 sec/step, 1 mm capillary, Ge (111) monochromator, and LiF (400) crystal analyzer. Peak positions were located (PEAKFIND), the pattern indexed (TREOR), systematic absences determined, individual reflection intensities extracted (ALLHKL), and direct methods applied (XTAL). The framework structure (right) has 4 Si and 7 O atoms in the asymmetric unit, and 9 of these 11 positions appeared in the direct methods solution. Eight were used to generate a difference Fourier map, which clearly showed the remaining three oxygen positions.

A whole-pattern, or Rietveld refinement of the structure (XRS-82) in the space group $I4_1/amd$ ($a = 10.2387(1)$ and $c = 34.3829(1) \text{ \AA}$) converged with $R_F = 0.100$, $R_{wp} = 0.225$, and $R_{exp} = 0.190$ (left). Neither of the two cages which make up Sigma-2 has been encountered before. The large cage is roughly spherical with a free diameter of $7.5 \text{ \AA}$ and 4 point symmetry. It can be visualized as a tennis ball with twelve 5-rings forming the seam and rows of four 6-rings filling in the spaces. The small cage, consisting of three 4-rings and six 5-rings, is new, but a relationship to a cage found in nonasil is apparent.

This work was sponsored by ICI in the form of a JRS grant with Dr. A.M. Glazer.

I thank Drs. D.E. Cox and M.M. Eddy for their assistance during data collection at the NSLS.

L. M. Moroney (NSLS), P. Thompson* (BNL), and D. E. Cox* (BNL)

By making use of the anomalous dispersion of x-rays close to the Zr and Y absorption edges we have found that individual cation B factors can be determined independently in a refinement of the structure of yttria-stabilized zirconia ceramic material with composition $Zr_{0.81}Y_{0.19}O_{1.90}$. With x-ray powder data collected at a single wavelength this is not possible because the two cations share the same set of sites and their B factors are highly correlated in any structure refinement. Normally only one average value can be determined. Simultaneous refinement of data collected at three different x-ray wavelengths (0.7726(1)Å, 0.7283(1)Å and 0.6892(1)Å) has allowed the determination of separate mean square displacements for each atom, the respective values being 0.45(2) for Zr^{4+} , 0.24(6) for Y^{3+} and 0.098(2) Å² for O^{2-} . The results indicate that the structural configuration of Zr^{4+} is significantly different from that of Y^{3+} .

Doping zirconia with aliovalent oxides such as Y_2O_3 enables the stabilization at room temperature of the cubic fluorite phase in which both the dopant and host cations occupy crystallographically equivalent sites. Electroneutrality is preserved by the creation of one anion vacancy in the lattice for every pair of dopant Y^{3+} ions. Existing crystallographic evidence indicates there is considerable static disorder in the material, particularly on the anion sublattice, although smaller cation displacements have also been observed.^[1,2,3] In the fluorite structure all atoms are on fixed positions and the specific structural parameters we wish to determine accurately are the effective Debye parameters (B) for the individual atoms.

The refinement of the combined data sets was carried out simultaneously with a model (I) for the calculated structure factors, F^2_{calc} , with three scale factors, K_A, K_B, K_C ; viz; $F^2_{obs}(A) = K_A F^2_{calc}(A)$, $F^2_{obs}(B) = K_B F^2_{calc}(B)$ and $F^2_{obs}(C) = K_C F^2_{calc}(C)$. The variables in the fitting process were Debye parameters for Zr^{4+} , Y^{3+} and O^{2-} and three independent scale factors, one for each data set. The latter

Table 1. Debye-parameters and Scale Factors

Model I: Debye-parameters for Zr and Y individually refined.

Model II: Debye-parameters for Zr and Y constrained to be equal.

Model I				Model II			
	B(A ²)	Scale	Factors		B(A ²)	Scale	Factors
Zr^{4+}	1.18(4)	K_A	0.0717(1)	Zr^{4+}	1.08(1)	K_A	0.0718(1)
Y^{3+}	0.64(15)	K_B	0.0758(1)	Y^{3+}	1.08	K_B	0.0757(1)
O^{2-}	2.57(4)	K_C	0.0458(2)	O^{2-}	2.57(4)	K_C	0.0460(2)

$$R_F = 1.7\%, R_{WF} = 1.8\%$$

$$R_F = 1.9\%, R_{WF} = 2.1\%$$

were necessary to account for the wavelength-dependent changes in the absolute intensities. Table 1 lists the refined values, their standard deviations and the estimates of the reliability of the fit. For comparison a model (II) with the cation Debye parameters constrained equal is also given. A Hamilton significance test [4] of the two refinements based on the weighted R-factors demonstrates that the inclusion of the extra parameter $B_{Y^{3+}}$ is significant at the 99.5% confidence level.

This technique has clearly enabled us to distinguish between the two cations of the shared sites with a significantly larger Debye parameter being obtained for Zr^{4+} compared to Y^{3+} . The excellence of the fit and the high quality data are indicated by the small R factors obtained and the small ESDs. To illustrate the effect of using all three datasets simultaneously, we performed the same refinement on the individual datasets. In this case, the correlation between the B factors of the Zr^{4+} and Y^{3+} ions was 100%, compared to 97% for the above refinement, and individual values could not be determined.

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Acknowledgment

Helpful discussions with D. P. Siddons and S. Heald are gratefully acknowledged. The sample of yttria-stabilized zirconia was kindly provided by Magnesium Elektron (U.K.). This work was supported by the U.S. Department of Energy Division of Materials Sciences and Division of Chemical Sciences (Contract DE-AC02-76CH00016) at Brookhaven National Laboratory.

DIFFRACTION STUDY OF A VANADIUM PHOSPHATE CATALYST FOR THE OXIDATION OF n-BUTANE TO MALEIC ANHYDRIDE.

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Mixed oxides of vanadium and phosphorus are known to act as heterogeneous catalysts in the oxidation of n-butane and n-butene to maleic anhydride¹. The catalyst is activated by exposing crystalline $(VO)_2P_2O_7$, to which an excess of phosphate has been added, to a stream of n-butane above 400°C. The resulting material is a mixture of crystalline $(VO)_2P_2O_7$ and an amorphous phase (or phases) of unknown composition and topology. The crystal structure of the catalytically important compound $(VO)_2P_2O_7$ has been reported². More recently a study by Bergeret *et al* concluded that the amorphous phase resembles β - $VOPO_4$. In order to test this conclusion, wide angle X-ray scattering data were collected, for both the unactivated compound (totally crystalline) and working catalyst (mixed amorphous and crystalline), at the X13A beam-line.

A Ge(220) crystal was used to monochromate X-rays ($\lambda=0.6898\text{\AA}$). Samples were in the form of pressed discs, enclosed in a chamber filled with helium and mounted on a Huber 4-axis spectrometer. An intrinsic Ge detector was used to detect the scattered photons. The structure factors determined for both samples were scaled appropriately and subtracted to give $\Delta S(Q)$, the difference structure factor due to the amorphous material in the working catalyst (Fig. 1).

Fig. 1. The difference structure factor derived by subtracting the structure factors for the working catalyst from that for the crystalline $(VO)_2P_2O_7$. The crystalline component of the working catalyst is broadened which results in the high frequency fluctuations.

The radial distribution function (RDF) was calculated by the direct Fourier transformation of the structure factor (Fig. 2). Comparison of this function with that calculated for known topologies (Fig. 3) suggests some relationship to structures containing corner-linked VO_6 -octahedra. However, the best qualitative match is for the RDF calculated for $VO(H_2PO_4)_2$ in which there is an excess of PO_4 -tetrahedra to VO_6 -octahedra over the 1:1 structures of α - and β - $VOPO_4$; hardly surprising since the working catalyst is produced with a ratio of P:V greater than 1:1.

Fig. 2. RDF derived from Fig. 1 of the amorphous component.

Fig. 3. RDF's calculated for the topologies of various vanadium phosphate compounds containing corner linked VO_6 -octahedra.

This work is in agreement with that of Bergeret *et al* in as much as it indicates that the amorphous phase contains corner-linked VO_6 octahedra as one of its structural elements. However, topologically and compositionally this material is more closely related to $VO(H_2PO_4)_2$ than it is to β - $VOPO_4$. Since these experiments do not allow us to extrapolate from a similarity in structural topology to some chemical relationship, they say little of the changes in or the distribution of the oxidation states of vanadium.

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PHASE STABILITY OF $\text{ZrO}_2\text{-Al}_2\text{O}_3$ FILMS GROWN BY MAGNETRON SPUTTERING UNDER APPLICATION OF PRESSURE

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Because of its high refractive index, high melting temperature, and corrosion resistant properties, zirconia, ZrO_2 , is a material with a wide vista of applications. Phase stabilized ZrO_2 has been used, inter alia, to prevent cracking in ceramics at elevated temperatures. The tetragonal phase of ZrO_2 , which can be formed at either high pressure or high temperature, can be retained by alloying with either Y_2O_3 or CeO_2 . Recently we have been successful in depositing $\text{ZrO}_2\text{-Al}_2\text{O}_3$ films and stabilizing the tetragonal phase of ZrO_2 with Zr:Al atomic ratios up to 0.76:0.24. For samples with higher ZrO_2 content, only the monoclinic phase of ZrO_2 was formed.

Standing films could be obtained by depositing the $\text{ZrO}_2\text{-Al}_2\text{O}_3$ mixture on a substrate of NaCl and then dissolving the latter in distilled water. In our earlier studies, we demonstrated that as-deposited films were all initially amorphous, but that by annealing in air at 1000° C, different polymorphs of ZrO_2 emerged.[1-3] The rate of crystallization was also found to be dependent on the $\text{ZrO}_2\text{:Al}_2\text{O}_3$ ratio; films with high Zr content crystallized in times as short as 2-h. In our earlier work, we noted that, in addition to particle size effects, a residual, internal compression was also possibly responsible for the stabilization of the high temperature tetragonal phase of ZrO_2 .

At room temperature, ZrO_2 has been found to transform from the room its normal monoclinic phase to a tetragonal phase at a pressure of about 5.0 GPa, and to an orthorhombic phase at about 15.0 GPa. We have investigated the high pressure behavior of films of two compositions: 64:36 and 45:55. In the case of the 45:55-sample, the tetragonal-to-orthorhombic phase change appears to be at about 3.4 GPa. Two additional diffraction peaks with d-spacings of 3.344 and 2.12 Å were tentatively identified as those of the orthorhombic phase with (100) and (112,022) Miller indices. In the case of the 64:36-sample, the tetragonal phase remains stable even up to 15.0 GPa. In an effort to induce crystallization with pressure, we subjected an initially amorphous 64:36-sample to 25.0 GPa pressure; there was no evidence of crystallization. The stability of the tetragonal phase of the zirconia films under application of pressure appears to be dependent on the Al_2O_3 composition. The amorphous films of $\text{ZrO}_2\text{-Al}_2\text{O}_3$ do not crystallize up to pressures of 25 GPa.

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HIGH PRESSURE STUDIES OF HgMnTe

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The ternary alloys $\text{Hg}_{1-x}\text{M}_x\text{Te}$, where $\text{M} = \text{Cd}, \text{Mn}, \text{or Zn}$, are important materials for their application in electro-optic devices and magneto-optic devices in the infrared range. In our earlier high pressure investigations, we examined the effects of alloying HgTe with Cd and Zn.[1-2] Interest in the HgZnTe-system arose from the theoretical prediction that adding Cd to HgTe would tend to destabilize the already weak HgTe-bond, whereas the addition of Zn would have the opposite effect.[3] We found that, in addition to the difference in the pressure dependence of the atomic volume, the stability of the two phases were in fact different. In both cases, the B3-to-B9 structural transition pressure, P_t , increased from that of pure HgTe. However, the effect of adding Cd was to increase the stability of the B1-phase, whereas the addition of Zn suppressed this phase.

Alloying with Mn is very appealing both because of its magnetic properties and the fact that it too will alter the HgTe band gap. However, it was not known whether Mn would stabilize or destabilize the HgTe bond and it is for this reason that high pressure experiments were performed on $\text{Hg}_{0.91}\text{Mn}_{0.09}\text{Te}$ at NSLS on the white beam line (X13-A) using standard energy dispersive diffraction and diamond-anvil cell techniques. [4]

The volume compressibility of $\text{Hg}_{0.91}\text{Mn}_{0.09}\text{Te}$ is, within the experimental uncertainty, equivalent to that of HgTe and $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$. The B3-to-B9 phase transformation was observed to occur at 2.3 ± 0.1 GPa; no B9-to-B1 transition was observed up to 10.0 GPa, but a transition from the B9 to the A5 phase was seen at 11.5 ± 0.5 GPa. Thus, the effect of alloying HgTe with Mn is similar to that of alloying with Zn in so far as the stability of the B1-phase is concerned, whereas the stability of the B3 phase is comparable with that of $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$. The volume compressibilities of all the materials, HgTe, $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$, and $\text{Hg}_{0.91}\text{Mn}_{0.09}\text{Te}$ are the same within the experimental uncertainty and the effect of adding Mn, Zn, and Cd to HgTe is to increase the stability of the zinc-blende structure under the application of pressure.

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X-RAY ANALYSIS OF PLASMA-SPRAYED PARTIALLY-STABILIZED ZIRCONIA

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Synchrotron x-ray radiation was employed on Beam Line X-13A to carry out a detailed analysis of the various phases (cubic, tetragonal and monoclinic) comprising a partially-stabilized zirconia; $ZrO_2-8\% Y_2O_3$, which is used as a "thermal barrier coating". The analysis of this material was carried out on powders (40 μm obtained from mechanically reducing fused product) and 300 μm thick plasma-sprayed deposits. Of special interest were the residual stresses thought to arise from the rapid solidification process inherent in plasma-spray deposition. In addition, specimens were thermally cycled and in some cases held statically at high temperatures. Only the as-deposited coatings are discussed here. Diffraction peaks were analyzed using a least ch-square method by a random parameter fit. A modified Gaussian equation with three parameters was assumed for a diffraction peak, as given in Fig. 1. Of special interest in this early period of study was the measurement of residual stress. The latter arises due to the difference in thermal expansion between the ceramic oxide coating and the metallic substrate. The failure of this system is generally believed partly due to stresses generated by expansion mismatch. Residual Stress Measurements: The (620) reflection was chosen for precise residual stress measurements. There are three diffraction peaks overlapping in the (620) region: Tetragonal (620); FCC (620); Tetragonal (602). X-ray scans were obtained in the (620) region. The first scan was performed with an inclined angle $\Omega=0.0$. For the second scan, the sample was inclined by $\Omega=45.0$. Diffracted intensity for the second scan decreased to 1/3 of that of the first. The (620) and (602) tetragonal and the (620) FCC peaks were deconvoluted from the experimental data with a precise Bragg angle for all three peaks: Fig.2. Conclusions: The residual stress in the tetragonal phase 45 degrees to the surface specimen is compressive 111 MPa. The residual stress in the cubic phase 45 degrees to the surface of the specimen is compressive 336 MPa.

Finally: FCC $\Delta d = d_i - d_n = 1.12 \times 10^{-3} \text{ \AA}$; for cubic phase
 Tet (620) $\Delta d = d_i - d_n = 3.7 \times 10^{-4} \text{ \AA}$; tetragonal phase
 Tet (602) $\Delta d = d_i - d_n = 4.4 \times 10^{-4} \text{ \AA}$; tetragonal phase

It can be concluded that synchrotron radiation is capable of determining the residual stresses within individual phases comprising the partially-stabilized ZrO_2 ceramic. This is an extremely important result and will enable the determination of anisotropy factors in thermal expansion of a range of thermal barrier coatings.

Fig. 1

Fig. 2

PRIMARY EXTINCTION IN NICKEL POWDER

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The powder diffraction beam line X13A was used to study the effects of primary extinction in powder samples. The line profiles of the first three reflections of Ni were measured from a series of samples using the wavelength of the characteristic CuK α radiation, 1.5418 Å. The samples were made of the same powder, but the compacting pressure varied from 6 MPa to 480 MPa. Special emphasis was put on careful recording of the very long tails of the reflections, extending the measurements up to 3 degrees (in 2 θ) on both sides of the peaks. The contribution of the thermal diffuse scattering (TDS) was removed by subtracting from the measured intensities the intensities of a well annealed sample, where the tails of the Bragg reflections are negligible. The intensities were brought to an absolute scale through a comparison with a standard sample (1). The intensity in the tails is

$$i(s) = N_{hkl} / 2\pi s^2 L, \quad (1)$$

where $s = (\cos\theta/\lambda)\Delta 2\theta$ is the distance from the peak, and

$$N_{hkl} = \int i(s) ds \quad (2)$$

For an analysis of the tails, another function is introduced (2),

$$G(s) = 2\pi s^2 i(s) / N_{hkl}, \quad (3)$$

so that the asymptotic value of G is $G_{as} = 1/L$. Here L is the volume average of the size of the diffracting domains in the direction of the scattering vector. The value of L was determined from the measured $i(s)$ for the different Ni samples.

The absolute integrated intensities of the reflection were also measured using a conventional x-ray source. The results were corrected for the effects of porosity and preferred orientation, so that the remaining differences were due to primary extinction. The primary extinction factor can be written as

$$y_p = \exp(-a^2(L/\Lambda)^2), \quad (4)$$

where Λ is the extinction length and a is a constant that depends on the shape of the diffracting domains (3). There is a good agreement between the observed y and L , if the domains are assumed to be plate-like. This is also the shape suggested by the electron micrographs.

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* Work supported by the Academy of Finland, project 01/545.

** Work supported by U.S. Department of Energy contract No. DE-AC02-76CH00016.

ELECTRIC FIELD INDUCED DISPLACEMENTS IN POTASSIUM TITANYL PHOSPHATE (KTP).

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Potassium titanyl phosphate (KTP) is a relatively new non-linear optical material which has recently attracted considerable attention because of its high non-linear coefficient, high optical damage threshold and low phase matching temperature sensitivity. These properties make KTP the premier material used for second harmonic generation of the 1.06 μ YAG laser. In addition, recent studies have shown that large single crystals may make excellent wave guides and electro-optic modulators.

Synchrotron radiation is an ideal probe for studying the effect of a polarizing field on the structure of these non-linear optical materials. The high resolution enables very small distortions in the unit cell to be measured (separations of $\Delta d/d$ less than 10^{-5} can be detected). In addition, because of the tuneable nature of synchrotron radiation the volume of the KTP crystal which is probed can be altered. Thus surface effects can be studied by using long wavelength X-rays.

The experiment undertaken on beam line X13b was to apply an alternating square wave potential across a crystal of KTP, while simultaneously measuring the peak profile of reflections along the polar axis. The potential and frequency could be altered and the counter was gated so that data for positive and negative polarization was collected.

Figure 1 illustrates the effect of altering the frequency of the alternating field on the intensity of the 080 reflection. The intensity difference decreases with increasing frequency. The cations find it more and more difficult to respond to the alternating voltage. At 100Hz, there is essentially no difference between the intensity of the 080 reflection when the field is +1000v or -1000v. The inertia of the potassium cations is such that they cannot respond quickly enough to this rapidly altering field.

Figure 1. Effect of frequency on the 080 reflection.

Figure 2. Effect of applied field on the 080 and 0120 reflections.

Figure 2 shows the effect of applied field on the intensity difference of the 040 and 080 reflections. In both cases a plateau is reached which presumably corresponds to a point where the attractive forces from the titanyl phosphate framework must be broken if the cations are to move further. Similar plots for the effect of increasing field and frequency on the unit cell parameters have been calculated.

Thus, from these measurements, the displacement of the cations (from the intensity variation) and the extension of the framework (from the unit cell distortions) can be monitored.

* Work supported by the Division of Chemical Sciences, U.S. Dept. of Energy, under contract DE-AC02-76CH00016

DATA COLLECTION FROM ECORI ENDONUCLEASE-DNA COCRYSTALS AT CRYSTALLOGRAPHY STATION X13B.
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The enzyme EcoRI endonuclease ($M_r=31,000$) binds as a dimer to DNA at the sequence 5'-GAATTC-3' and, in the presence of magnesium, hydrolyzes the phosphodiester bond between guanine and adenine on each strand. The crystal structure of the complex between endonuclease and a cognate oligonucleotide (5'-TCGC-GAATTC-GCG-3') was solved previously to 3A resolution (1). Cocryystals are obtained in the absence of magnesium, and are hexagonal plates with space group P321 and unit cell $a=b=118.4\text{\AA}$, $c=49.7\text{\AA}$. The enzyme within these cocryystals can be activated by soaking them in a magnesium buffer: the DNA undergoes double-strand cleavage yet the crystals remain intact. In order to determine structural changes after DNA hydrolysis and to search for Mg sites, we collected a complete data set for Mg-soaked cocryystals. Average crystal size was $.6 \times .6 \times .2 \text{ mm}$. An Enfrap-Nonius oscillation camera with a 0.2 mm collimator was used to collect 90 degrees of film data at room temperature. Crystal to film distance was 100 mm, and the wavelength was 1.576 $\text{\AA}$. A 2 degree oscillation range was used (camera speed = 5 sec/deg) with total exposure time of 20 min per film (see Fig. 1). Since a large number of crystals was available, each was used to generate only 3-4 films (or fewer if radiation damage became visible). Two Polaroid exposures of 3-5 min each were used to align each crystal. During data collection, the ring current was in the range 70-180 mA.

We have recently grown cocryystals containing EcoRI endonuclease and longer DNA (5'-TCGTG-GAATTC-CACG-3') with different base pairs flanking the recognition site. These crystals are triangular plates with space group R32 and $a=b=127\text{\AA}$, $c=146\text{\AA}$. Complete data was collected for these "15-mer" cocryystals. The average crystal size was $.4 \times .4 \times .2 \text{ mm}$ and collection parameters were similar to those already described (see Fig. 2). Also, partial data was collected for a gold derivative of this crystal form.

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Fig. 1. 2° oscillation photograph for an EcoRI endonuclease - tridecamer DNA co-crystal soaked in magnesium. Maximum resolution is about 2.9 $\text{\AA}$.

Fig. 2. 2° oscillation photograph for an EcoRI endonuclease - 15mer DNA cocrystal. Maximum resolution is about 3 $\text{\AA}$.

This work supported by NIH grant GM25671 to J.R.

SYNCHROTRON X-RAY SCATTERING IN AN EXTERNAL ELECTRIC FIELD

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The organic crystal MNA (2-Methyl-4-Nitro Aniline, non-centrosymmetric space group (Cc) is well known for its large non-linear optical properties (linear electro-optical component $r_{111} = 67 \times 10^{-12}$ m/V).¹ In order to better understand the microscopic origin of these effects, an X-ray scattering experiment has been performed at beamline X13B of the National Synchrotron Light Source. The experiment gives, for the first time, information on molecular polarizability at the atomic level.

An alternating electric field (50 Hz, 10 kV/cm) has been applied along the MNA polar axis. The counting signal was gated to separately record the "field up" and "field down" scattered intensity. 21 reflexions were collected with this "modulation method".²

Preliminary results show a significant change in the scattered intensity ($(\Delta I/I)_{\max} \approx 3\%$). Two possible origins for the observed effect have been investigated. They are a molecular polarization and a piezoelectric effect which through a rotation of the molecule affects the unit cell constants. Refinements using newly modified programs indicate that both effects may contribute. The induced dipole moment is about 0.1 D according to our present data, while the molecular rotation is only a few hundreds of a degree around an axis perpendicular to the long axis of the molecule.

This experiment is to be continued when NSLS resumes operation.

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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.

EXPERIMENTAL PHASE DETERMINATION OF CRYSTALLOGRAPHIC STRUCTURE FACTORS BY MULTIPLE SCATTERING TECHNIQUES

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The solution to the "phase problem" in crystallography has been essential to the rapid growth of structural information. Presently this problem may be solved by statistical methods for structures involving < 150 atoms or by heavy-atom substitution methods for macromolecules. It has however long been realized that the details of the coherent interaction of the diffracted beams from several Bragg reflections simultaneously scattering contain phase information of the reflections involved. The inherent collimation and tunability to long wavelengths of synchrotron radiation suggest a possibility of convenient direct experimental determination of the phases. Initial studies of single crystals of Si and $\text{Ge}_{38}\text{As}_{81}\text{I}_9$ at the Crystallography Beam Line X-13B clearly demonstrated the feasibility for direct experimental phasing.

The experiments were performed at several wavelengths by recording the multiple diffraction peaks obtained by rotating around the $(222)(\text{Si})$ or $(022)(\text{Ge}_{38}\text{As}_{81}\text{I}_9)$ scattering vectors. The resolution in the ψ -scans were typically 0.005° per step. The figure illustrates the dynamical three beam interaction in Si displaying the asymmetry around the central peak (truncated in the figure). The nature of the asymmetry (dip and slow descent) yields the phasing information.

COUNTS

Details of a simultaneous reflection peak profile involving Si_{222} . The peak intensity is 60000 counts and its FWHM $\leq 0.02^\circ$. $\lambda = 1.325 \text{ \AA}$.

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.

STRUCTURAL STUDIES OF AMORPHOUS CHALCOGENIDE SEMICONDUCTORS

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The determination of the atomic structure of amorphous (a-) semiconductors has long been a much sought after but seldom attained goal. For example, several models have been proposed for the structure of the well-characterized material a-As₂S₃. An important factor which contributes to this lack of agreement among the proposed models is the method of preparation. Indeed our previous study of the effect of quenching temperature on the structure of stoichiometric bulk glasses has demonstrated¹ that the structure of glassy (g-)As₂S₃ is not unique. Preliminary x-ray diffraction measurements for a family of samples of bulk-quenched g-As₂S₃ were performed on beamline X-13B at the NSLS. In this work we focus on the first sharp x-ray diffraction peak at low scattering factor about 1.2 Å⁻¹. By coupling these results with structural models², we hope to ascertain more completely the intermediate range structural modifications associated with the quenching temperature effect in g-As₂S₃.

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NOTE: This research was supported by the U.S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences under Contract Nos. DE-AC02-76CH00016 and DE-AS05-80-ER10742 and by the National Science Foundation under Grant No. DMR-8407265.

SAMPLE DAMAGE AT BNL/NSLS ON BEAM LINE X9-A

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Introduction

Our aim was to study the structure of enzymes and their functional intermediates during turnover under physiological temperature using x-ray absorption spectroscopy. One problem that arises as a result of prolonged x-ray irradiation of biological samples is the sample damage (whether reduction by hydrated electrons or other damage). A systematic study of the sample damage is essential. Our preliminary results are reported here:

We have performed two types of experiments: a) the sample was flowing through a sample chamber and its redox state was monitored optically using a simple single beam spectrometer, b) static samples were exposed to the x-ray beam for certain amounts of time, and later their optical and ligand binding properties were studied.

Results and Discussion

Experiment 1: The sample chamber was placed at 45° with respect to the x-ray beam. The sample was circulated through the chamber from a reservoir at a rate of 10 ml/min. using a peristaltic pump. Three proteins were used in this experiment: oxidized cytochrome c, met myoglobin and cytochrome c oxidase. We monitored the redox state at the following wavelengths: cytochrome c-550 nm, met myoglobin-635 nm, cytochrome oxidase-445 nm. The results did not show any substantial change at 550 nm for about two hours. After exposure to radiation excess dithionite was added to fully reduce cytochrome c. The sample was frozen quickly at -80° C. Later, this x-ray irradiated sample was passed through a sephadex G25 column to remove excess dithionite, and its electron donating capability to cytochrome oxidase was measured. The maximum turnover number with respect to oxygen was found to be 39 sec⁻¹ as compared to 37 sec⁻¹ for a control sample. Thus, we conclude that no substantial damage of cytochrome c was observed for about two hours of x-ray irradiation corresponding to 3.6 x 10¹² photons. Met myoglobin was similarly exposed to x-ray beam for about 1 hour. There was no observable reduction during this period. After completion of the experiment, excess dithionite was added and frozen at -80° C. The optical spectra of this deoxy state and later carbonmonoxy liganded state were identical to a control sample.

Cytochrome oxidase was also tested for x-ray induced damage. For about 2.5 hours, there was no substantial reduction, however some reduction was observed after 2.5 hours. When the beam was turned off, we noticed a partial reoxidation. But later testing (CO binding capacity) suggests that cytochrome oxidase was damaged as it did not bind any CO, as judged from the spectral changes in the alpha region.

Experiment 2: Two different systems were employed as follows:

A) Aqueous Samples: Cytochrome oxidase of different concentrations (80, 100 µM) in phosphate buffer (0.1 M, pH 7.0) was exposed to synchrotron radiation (NSLS,BNL) for two and a half hours at 40-45 mA. The radiation damage was determined by measuring the ratio of the absorption at 605/655 nm. The ratio was found to be increased after irradiation.

B) Dry Film Mounted Samples: The radiation damage of the enzyme was determined by measuring the absorption of 605/655 nm. In dry PVA film mounted samples the ratio decreases after irradiation. The unusual behavior of the enzyme in dry film mounted samples cannot be easily explained. However, these results indicated that the redox effects of hydrated electrons is predominant in aqueous samples whereas no such effect is implicated in dry film mounted samples.

These results imply that prolonged exposure not only reduces (by hydrated electrons) but also damages the samples. Hence, further studies will be conducted to investigate the following:

- 1) Sample damage at sub-zero temperatures.
- 2) Protection of the sample by physical and chemical means.

Physical

- a) changing dose-rate
- b) changing the exposure time
- c) limiting the number of scans for each sample

Chemical

- a) scavenging of radicals by non-thiol compounds, e.g., formate, ethanol, DMSO, etc.
- b) scavenging of radicals by thiol compounds

This work was carried out on Beam Line X9-A, supported by NIH Grant RR-01633, and this work was supported by Grants HL-18708, DMB-8414521, HL-31909, GM-31992 and GM-33165.

COMPARISON OF THE ACTIVE SITE MANGANESE IN MANGANESE SUPEROXIDE DISMUTASE AND MANGANESE CATALASE

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Organisms that proliferate in the presence of oxygen have developed a series of enzymes to deal with the deleterious effects of reduced oxygen species such as the superoxide radical anion (O_2^-) and hydrogen peroxide (H_2O_2). The role of manganese in the biological detoxification of these species has been appreciated only in the last several years. This laboratory has been interested in the role of manganese in catalytic dismutation of these reduced oxygen species since we reported the discovery of a manganese containing superoxide dismutase (MnSOD) in *E. coli* B in 1970 (1). Our continued interest in manganese containing enzymes resulted in the isolation and characterization of a novel manganese containing catalase (MnCAT) from *L. plantarum*. The active site manganese in the MnSOD has been studied using visible absorption spectroscopy and nuclear magnetic resonance spectroscopy (2). The data is consistent with the presence of Mn(III) in the resting state of the enzyme. A mechanism which involves alternate oxidation and reduction of the manganese during the catalytic cycle was proposed:

The visible absorption spectrum of the MnCAT is similar to MnSOD suggesting that the MnCAT also contains Mn(III) at the active site of the enzyme. However, unlike the MnSOD which contains one Mn per subunit, the MnCAT contains two atoms of Mn per subunit (3). Recent studies using electron spin resonance, suggested the possibility of a binuclear manganese cluster as the active component of the MnCAT. EXAFS will allow us to determine if a binuclear cluster is present and to estimate a distance of separation between the two Mn atoms. In addition, we should be able to determine the oxidation state of the Mn atoms in the resting form of the enzyme. We have also been successful in obtaining an inactive form of the enzyme that is stable to the desired measurements. Similar measurements on this inactivated preparation will be important to understanding the catalytic cycle of the enzyme.

Although there is substantial similarity in the visible absorption profiles of the two enzymes, there is no overlap in substrate specificity (4). Thus, the MnSOD is not a catalyst of hydrogen peroxide dismutation, nor is the MnCAT capable of dismuting superoxide. The information obtained from EXAFS measurements of these two enzymes will allow us to make a comparison of the active site manganese and perhaps provide some clue to a better understanding of the substrate specificity of these proteins.

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This work was supported by research grants from the Council for Tobacco Research, U.S.A., Inc.; the United States Army Research Office; the National Science Foundation; the Institute of General Medical Sciences of the National Institutes of Health; and the University City Science Center under the Biotechnology Resource Program of the Division of Research Resources of the National Institutes of Health.

X-RAY DIFFRACTION STUDIES OF MULTILAYER FILMS

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I. Meridional X-Ray Diffraction From Ultrathin Multilayer Films

Partially as a test of the photon flux density and focus produced by the current optics of Beam Line X9-A (Si(111) double-crystal monochromator and a variable, cylindrically-bent Al/Ni mirror), we have recorded (in November, 1986) the meridional x-ray diffraction from Langmuir-Blodgett multilayers containing from 1-10 bilayers deposited on flat, alkylated glass substrates utilizing multilayer oscillation and both one-dimensional and two-dimensional position-sensitive detectors. The photon flux density at 7605 eV was measured (via extrapolation to zero attenuation of the integrated intensity of the (002) Bragg reflection from a five-bilayer multilayer calibrated with a rotating-anode x-ray source and cylindrically-bent Ge(111) optics) to be $\sim 5 \times 10^{10}$ /sec/mm² within 0.1 mm of the vertical beam profile FWHM ~ 0.5 mm for storage-ring parameters 2.5 GeV, 105 mA. The line-focused beam produces ΔQ_z resolution more than sufficient to resolve all subsidiary maxima about the (002) Bragg peaks for the ten-bilayer multilayers with a multilayer period along z of 56Å. Resonance x-ray diffraction effects from barium about the Ba L_{III} absorption edge on the meridional diffraction from five-bilayer multi-layers of barium arachidate have been utilized to determine the positions of the barium atoms within the multilayer profile to ± 1 Å accuracy. This work was sponsored by the NIH (Grants GM-33525 and HL-18708) and the NSF (MRL Program Grant DMR-8519059).

II. Non-Resonance and Resonance X-Ray Diffraction Studies on Protein Monolayers and Thick Membrane Multilayers

Two different experiments were performed (in February, 1987) on Beam Line X9-A employing a Si(111) double-crystal monochromator, a variable, cylindrically-bent Al/Ni mirror, a Huber 4-circle diffractometer and a linear position-sensitive detector. The first investigated the resonance scattering effects from iron on the meridional diffraction from a single monolayer of cytochrome c on the surface of a five-monolayer multilayer of arachidic acid on a flat, alkylated substrate over a ± 100 eV energy range about the FeK absorption edge (7110 eV) to a spatial resolution of 5Å. The second investigated the nature of the non-resonance meridional x-ray diffraction from thick multilayers of functional sarcoplasmic reticulum membranes over the energy range from 7000 eV to 4000 eV. Results from the former experiment have been utilized to determine the profile structure of this non-periodic, ultrathin multilayer to 5Å - resolution (previously determined to 10Å - resolution employing a rotating-anode source) and the position of the cytochrome heme iron atom within this profile structure to ± 1 Å. Results from the latter experiment clearly demonstrated the feasibility of performing resonance x-ray diffraction on calcium bound to the two high-affinity binding sites of the Ca²⁺ ATPase within the sarcoplasmic reticulum membrane profile structure. This work was sponsored by the NIH (Grants GM-33525 and HL-18708).

The National Biostructures PRT and Beam Line X9-A are supported by NIH through the Biotechnology Resource Program of the Division of Research Resources under Grant RR-01633 and the NSF under the MRL Program Grant DMR-8519059.

STUDIES OF MULTIPLE SCATTERING IN XANES: BEAM LINE X9-A

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In recent years it has become apparent that the XANES is more similar to EXAFS than was previously supposed. Of critical importance in this connection is the dependence on energy of photoelectron multiple scattering (MS) relative to single scattering (SS). If MS decays rapidly enough with energy, EXAFS-like analysis methods should be applicable in the low-k region. We have recently completed what we believe is the first really "clean" experiment to address this issue. Previous studies have used condensed matter samples, and SS contributions from distant atoms are difficult to distinguish from MS from near atoms. By using Germanium gases GeH_4 , GeH_3Cl and GeCl_4 we have been able to clearly separate these effects, and reaffirm previous conclusions of Bunker and Stern (from studies of KMnO_4) that the "type 2" MS dies away rapidly past the edge. We have also performed a series of multiple scattering computer calculations on these and other systems. Although these calculations are very interesting, in our opinion the theoretical results are too sensitive to the details of the constructed atomic potentials to be used for quantitative structure determination at this time. We believe that previously reported XANES simulations of hemoglobin have been overinterpreted. Nevertheless the calculations are of considerable heuristic value, and we are trying to improve the methods.

Supported by NIH through the Biotechnology Resource Program of the Division of Research Resources under Grant RR-01633.

BEAM LINE X9-A END STATION INSTRUMENTATION: SPECTROSCOPY

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The essential basic equipment is in place for conventional two channel fluorescence mode EXAFS/XANES experiments. Although initial testing of the instrumentation showed the equipment to be generally adequate, it also revealed some (usually minor) deficiencies and problems which we are now attempting to remedy. Precise manual and/or computer controlled apertures (slits) currently are provided to define x-ray beam dimensions. Incident intensity is monitored using a transmission type ionization chamber, or a scatterer with a ZnS scintillator/photomultiplier tube detector. For fluorescence detection the PRT owns one Stern/Heald Type fluorescence ion chamber with Soller slits, low noise preamp, amplifier, and V/F converter. Available gains are 10^{10} , 10^{11} and 10^{12} volt/amp. Also present on the beam line are: 5" diameter ZnS detectors, one Keithley 427 amplifier, dual channel 100 KHz/V voltage-to-frequency converter module, and X-Z translation stages. One 6 channel scaler is installed in the computer interface, so that 5 detectors can be monitored at once when enough V/F converter modules are built. "User friendly" data acquisition software for routine EXAFS experiments has been written and tested. A solenoid driven attenuator has been built to help perform routine tests for nonlinear response of the whole detection system. A simple but general purpose "dual signal switcher box" was also constructed to interface an arbitrary "two state" experiment (e.g., light on/light off for photosensitive materials) to the computer without reprogramming. Construction of additional test and calibration equipment is planned.

Existing equipment is being modified to improve its operating characteristics and reliability, and new equipment is being built to improve experimental flexibility and reduce down time on the beam line. Highest priority is given to constructing accurate, reliable, easy to use and documented equipment for the most common experiments. A separate core research project is devoted to pushing the state of the art in EXAFS instrumentation.

Supported by NIH through the Biotechnology Resource Program of the Division of Research Resources under Grant RR-01633 also RR-05823 (Biomedical Research Support Grant).

RAPID FLOW EXPERIMENTATION ON BEAM LINE X9-A

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The test program involves alignment, signal acquisition effectiveness, interference of x-ray and optical signals, sample damage, sample flow rates, sample concentration evaluation. The regenerative flow apparatus was tested with Fe EDTA, metmyoglobin and horseradish peroxidase for an interval of four hours. In this interval of continuous running at 50 msec times resolution, the protein was denatured by 10%. Improved pistons are expected to give at least one shift of running time at a time resolution of 100 msec and a concentration of 0.7 mM.

MD 557(de)

Drawing(right) and Photograph(left) of Regenerative Flow Apparatus for X-Ray Absorption Spectroscopy

This work was carried out on Beam Line X9-A supported by NIH under Grant RR-01633, and this work was supported by Grants GM-31992, HL-18708 and GM-33165.

STRONG INCOMMENSURATE FLUCTUATIONS IN A SMECTIC-A PHASE

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The synthesis of rod-shaped organic molecules having fixed, permanent dipole moments has led to a rich variety of liquid crystal (LC) phases. Most polar smectic phase diagrams can be successfully interpreted in the frame of a phenomenological model² for a frustrated smectic with two order parameters $\Psi_1(\vec{r})$ and $\Psi_2(\vec{r})$ (often identified as the dipole moment density and the center of mass density waves) that individually would condense at two incommensurate wavevectors k_1 and k_2 with $1 < k_2/k_1 < 2$. Depending on the choice of parameters, this model can describe a monolayer A_1 phase, a bilayer A_2 phase (in which $k_1 = k_2/2$), a partial bilayer A_d phase, and two-dimensional A and C phases in which two vectors of length $k_1 > k_2/2$ sum to form a vector of length k_2 . Quite naturally, the theory also predicts a stable uniaxial incommensurate phase smectic- A_1 , in which two colinear modulations of incommensurate wavelength are simultaneously condensed, producing sharp scattering peaks at k_1 and k_2 .

In contrast with ordinary incommensurate systems, in an incommensurate LC it is difficult to distinguish between the "ordered" and "modulating" periodicities, since both potentials may be comparable in strength (i.e. Ψ_1 and Ψ_2 may be comparable in amplitude). However, there is still a distinction between weakly coupled phases, which presumably consist of interpenetrating density waves and yield Bragg peaks at k_1 and k_2 only, and strongly coupled phases, which may be considered as consisting of a periodic array of solitons, and will peak at all sums $q = nk_1 \pm mk_2$.

Weakly coupled incommensurate phases have previously been reported in smectic phases³. We have made high resolution x-ray scattering measurements on a liquid crystalline smectic- A_1 phase, which show two diffuse maxima at incommensurate wavevectors in addition to a fundamental quasi-Bragg peak. These diffuse peaks indicate the close proximity of an incommensurate phase with two strongly coupled parameters. The material studied was a mixture⁴ of DB₅ with 22.88 molar % T₈. The sample cell oven and scattering geometry were as described previously⁵. X-ray diffraction data were taken at NSLS port X9a utilizing a double crystal Si(111) monochromator and matching analyzing crystal, with a longitudinal resolution $\Delta q = 0.00012 \text{ \AA}^{-1}$ FWHM.

Figure 1 shows plots of scattering intensity as a function of $q_{||}$, the momentum transfer along the orienting magnetic field, at a variety of fixed temperatures. The solid lines are the results of least-squares fits to a sum of Lorentzians. With descending temperature, the following phases are seen: a nematic (N) phase above 124.5°C, a partially bilayer A_d phase between 120 and 124.5°C, a monolayer A_1 phase between 119 and 113.5°C, and a true bilayer A_2 phase below 110°C. The A_d and A_1 , and the A_1 and A_2 phases are separated by coexistence regions.

The A_d phase displays two sharp scattering peaks at $q_0' = 0.131 \text{ \AA}^{-1}$ and $2q_0'$, and two additional two diffuse maxima at 0.11 and $0.238 \text{ \AA}^{-1}$, signaling fluctuations toward the A_1 phase. The A_1 phase, by contrast, has a sharp peak at $2q_0 = 0.2380 \text{ \AA}^{-1}$ and diffuse maxima at q_0' and $q_- = (2q_0 - q_0')$. The widths of the q_0' and q_- peaks

Fig. 1) Scattering intensity collected along $q_{||}$ (parallel to the molecular long axis) at indicated temperatures (C) Note semilogarithmic axes.

are indicative of fluctuations into small smectic-like ordered regions with approximate size $\xi_{||} = 200-300 \text{ \AA}^{-1}$. These large fluctuations indicate the close proximity of an incommensurate smectic- A_1 phase, and the presence of the q_- "modulation" peak indicates that this must be a strongly coupled phase as discussed above. In a pure A_1 phase, of course, all peaks would be simultaneously resolution limited. Other peaks, ($2q_0 + q_0'$) for instance, have not been seen and are probably too weak to measure.

Footnotes and References

1. This work was supported by NSF-LRSM Grant No. DMR-85-19059. We thank the Institute for Structural and Functional Studies for their help at Brookhaven NSLS Port X9a, supported by NIH Grant No. RR-0163.
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LARGE AREA RECTANGULAR DETECTORS FOR XAFS SPECTROSCOPY

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Introduction

The beam size at Beam Line X9-A is 0.5 cm x 15 cm. A total flux of $10^{12} - 10^{13}$ photon/sec/eV band pass at 16 m from the source can be obtained for 2.4 GeV electron energy and 100 mA beam current. For this flux photon counting has its limitations. More so for the reason that in the future, some percentage of the NSLS x-ray operation will be in a single bunch mode. Large area sample holders are used for this beam size, and we use an array of 16 detectors for photon fluorescent signal collection in the integration mode. These detectors use ZnS(Ag) as scintillators mounted on a rectangular Hamamatsu Photomultiplier Tube (PMT).

Experiment

The R1612 rectangular PMT of area 88 mm x 40 mm was used for these detectors. Four such PMTs were placed in a row, they were enclosed in a box to avoid light leak. A mozzle in front was attached for mounting filters and for minimizing the astray radiation (Fig.1).

5 mM of Fe-EDTA solution was used in the cell. An array of 4 detectors was placed on top and the same number at the bottoan of the sample in front, and the same arrangement of detectors was made at the back of the sample (Fig. 2). The detectors were so arranged that the direct x-rays were going between these detectors, and the detectors only see the scattered and fluoresent signal photons. To minimize the scattering we use Z-1 filters (Mn in this case) close to the sample.

Results

The counts were recorded below the edge at 7.080 KeV and above the edge at 7.180 KeV. The beam current was 73 mA at 2.4 GeV. The average of the signal photons at the top and bottom at the front and at the back were recorded. It was found that as much as 28% of the signal photons were present at the back of the 2 mm thick sample as compared to 100% at the front.

SK 9

Fig. 1:

Fig. 2:

ELIMINATION OF X-RAY BEAM FLUCTUATIONS FOR X-RAY ABSORPTION STUDIES

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Introduction

X-ray beam line fluctuation is a common problem at almost all of the beam lines at different synchrotrons of the world. At NSLS the Pick-Up Electrodes (PUEs) correct the vertical and horizontal orbit of the electrons in the ring, and their sensitivity is not better than ± 100 microns in both directions. We built a device to reduce these fluctuations to less than ± 30 microns at the experimental station. This improves the data quality and saves the collection time.

Experiment

A wooden reed with ZnS(Ag) phosphor gives 120 Hz light spikes picked-up by a detector (R-signal). When the mean position of the reed is at the center of the x-ray beam, the spikes are equal in phase. A fluctuation in the beam gives a phase change and consequently a vertical track voltage, proportional to the phase change. This voltage drives a motor which brings the sample, the fluorescent detectors (giving M-signal) and the reed back to the central position of the beam (Fig. 1). The integrated measure of R and M gives the x-ray absorption spectrum.

Results

Fig. 2 shows the comparison of the feedback closed and opened. The plot was taken in a non-scan mode with a time constant of one second. The 6 minutes interval of 100 microns disappear in the closed loop. In average the sample was never deviated from the mean position of the x-rays by more than ± 30 microns, and for the practical beam fluctuations of a smaller amplitude, the time response was a fraction of a second.

Fig. 1:

Fig. 2:

Beam Line X9-A is supported by NIH through the Biotechnology Resource Program of the Division of Research Resources under Grant RR-01633 and this work was also supported by Grant CA-41787.

EXAFS STUDIES ON CARDIAC CYTOCHROME c₁

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EXAFS experiments were performed on Beam Line X9-A at room temperature on 1-2 mM solutions of oxidized and reduced cytochrome c, beef heart cytochrome c₁ ("one band" c₁), and a complex ("two band" c₁) of cytochrome c₁ with the "hinge protein", which mediates binding between cytochrome c and cytochrome c₁ into the active electron transfer complex in vivo. The cytochrome c spectra agree well with previous measurements made at SSRL and CHESS, the c₁ spectra were much better than those previously obtained at CHESS. Edge shifts upon reduction are consistent with those previously observed. The most interesting result of these experiments is that XANES and EXAFS spectra indicate that significant stereochemical changes occur upon binding of the hinge protein. An unusual double peak appears in the XANES of the two band c₁, which is reproducible between experiments and is not observed in one band c₁ or cytochrome c spectra measured under the same conditions. Analysis is in progress to quantitatively determine the bond lengths and Debye Waller factors. Future experiments will be necessary to obtain spectra of improved signal-to-noise ratio on frozen samples and to investigate the effects of possible radiation damage.

X-RAY ABSORPTION INVESTIGATION OF STEREOCHEMISTRY OF CYTOCHROME c' ON BEAM LINE X9-A

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EXAFS experiments were performed at room temperature on oxidized and reduced pH 7 samples of cytochrome c' from the bacteria *Rhodospirillum Rubrum* and *Molischianum* as well as appropriate model compounds and metazidohemoglobin. Unlike cytochrome c, Fe in cytochrome c' is known to have no sulfur ligands. Cytochrome c' exhibits characteristic changes in spin state as a function of pH, and under certain conditions an unusual "quantum admixed" intermediate spin state. The spectra on Beam Line X9-A were compared with data previously obtained at CHESS on frozen samples of the *Rubrum* protein at pH 7, 10 and 12. No significant differences were observed between the proteins from the two species of bacteria. The first shell data have been thoroughly analyzed, and a chemically reasonable picture of the heme environment as a function of pH and redox state has emerged. A manuscript is in preparation.

Beam Line X9-A is supported by NIH through the Biotechnology Resource Program of the Division of Research Resources under Grant RR-01633, and this work was supported by GM-32692.

TITANIUM XANES AND EXAFS OF SOME SILICATE MINERALS

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INTRODUCTION

The focus of this experiment is to obtain Ti site information for acmite ($\text{NaFe}(\text{SiO}_3)_2$) and kaersutite ($(\text{Ca},\text{Na}(\text{Mg},\text{Fe}^{++})_4(\text{Al},\text{Fe}^{+3},\text{Ti})_8\text{O}_{22}(\text{O},\text{OH})_2$), which have 5 weight % and 7 weight % TiO_2 , respectively. Titanite ($\text{CaTiO}(\text{SiO}_4)$) was used as the model compound, where Ti is in an octahedral site having 5 Ti-O distances ranging from 1.97 to 2.05 Å, and one shorter Ti-O distance at 1.77 Å. Considerable difficulty was encountered for the above samples at S.S.R.L., due to the low TiO_2 concentrations and significant air absorption of X-rays with energies near the Ti K-absorption edge (4960 eV).

EXPERIMENTAL

The samples consisted of particles less than one absorption length (approximately 30 microns) in diameter, that were deposited as one layer on tape. The experiments were carried out in fluorescence geometry, having ion chambers for the I_0 and I_f detectors. A NaIO_4 filter was placed between the sample and I_f chamber to improve signal-to-background levels for the Ti spectra. The Fe, and especially, the Ti data are surprisingly good, considering that no special provisions were made in the experimental set-up to reduce air absorption of X-rays.

RESULTS

Initial results indicate similar octahedral Fe environments for acmite and kaersutite. The Ti data were altered near the middle of the EXAFS range due to absorption of the coherent background from the L_1 edge of Iodine (5190 eV) from the filter. This effect is more pronounced for the samples having lower Ti concentrations (see Fig. 1). The resulting χ data extend out to only $7.5 \text{ \AA}^{-1}$. However, some quantitative interpretations can be made from the raw data and χ data.

The general frequency of the EXAFS oscillations are roughly the same for all three Ti samples, indicating octahedral Ti for all three samples. The kaersutite data indicate Ti in a more distorted or disordered site than Ti in titanite or acmite, since the pre-edge feature is stronger in the kaersutite Ti edge (see Fig. 1). From using the ratio method, the kaersutite Ti site is considerably more disordered than the Ti site in titanite, and is made up of two distributions of coordinating oxygens. One distribution accounts for approximately 30 % of the oxygens surrounding the central Ti at 0.18 Å shorter distances than the average Ti-O distance for Ti in titanite; and the other distribution accounts for 70 % of the oxygens in a much broader distribution of distances from the Ti.

Fig. 1. Ti K-absorption edge and EXAFS; all data were pre-edge background subtracted; and the edge-steps were normalized to one. The spectra were then offset for the plot.

Beam Line X9-A is supported By NIH Through Grant Number RR-01633.

CONTINUOUS ENERGY SCAN OF THE DOUBLE CRYSTAL MONOCHROMATOR ON BEAM LINE X9-A

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The rotary table which serves as the Bragg-angle drive of the double crystal monochromator was originally driven by a stepper motor. We have replaced the stepper motor by a digitally controlled DC-motor. Position feedback to the control electronics is by an encoder mounted on the input shaft of a 200:1 gear reducer, the output of which drives the rotary table.

We have recorded EXAFS-spectra in step scan mode (Fig. 1), i.e. the DC-motor is driven to the next desired energy position and is then stopped. After the usual settling time, data accumulation is started. We have also recorded an edge spectrum in continuous scan mode (Fig. 2), i.e. the DC-motor is continuously running at a low speed. Data are accumulated for a certain time and are then read out together with the energy position at that moment. Immediately after readout, a new data accumulation cycle is started.

The removal of the vibration generating stepper motor has resulted in improved quality of the EXAFS-data in step scan mode (Fig. 1). The data in continuous scan mode are of at least as high quality. The elimination of the customary settling time of a few tenths of a second will greatly improve the duty cycle of data collection.

The resolution of the encoder is 4096 quadrature step per revolution which gives 409600 quad-steps per degree of Bragg-angle. In step scan mode, the DC-motor reached the desired position within 5-8 quad-steps corresponding to less than 0.1 arc sec at the monochromator crystal. This is a better resolution than the 400 half-steps of the stepping motor. Repeats of scans in continuous mode (Fig. 2) differed by less than .02 eV at 6.5 KeV corresponding to 0.2 arc sec.

The improvement due to the "smooth running" DC-motor is demonstrated by the noise pattern of the monochromatic flux (Fig. 3). Besides the very small dip when the motor is turned on, there is no difference in the noise when the motor is at rest or running.

Fig. 1:
EXAFS-spectrum of KMnO_4
Monochromator is driven by a digitally controlled
DC-motor. The pattern was recorded in step scan mode.

Fig. 2:
Edge spectrum of KMnO_4 in continuous scan mode
Same monochromator drive as in Fig. 1.

Noise pattern of the monochromatic flux
Fig. 3: Same monochromator drive as in Fig. 1.
The arrow indicates when the motor was turned on.

VANADATE INHIBITION OF 3-PHOSPHOGLYCERATE KINASE

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3-Phosphoglycerate kinase catalyzes the following reaction in glycolysis:

High resolution structures for the enzyme isolated from horse muscle (1) and from yeast (2) have been obtained from x-ray diffraction data. The enzyme crystallizes in an open conformation in which the two domains that make up the active center are too far apart to allow reaction (1,2). The two domains are believed to come together during catalysis. Like several other enzymes that catalyze phosphotransfer reactions, 3-phosphoglycerate kinase is inhibited by vanadate (3). The especially potent inhibition of vanadate with this group of enzymes is attributed to the ability of pentavalent vanadium to adopt a stable trigonal bipyramidal geometry that is analogous to the transition state geometry in phosphotransfer reactions (4,5). Recent studies (6) have shown that vanadate forms a stable complex with 3-phosphoglycerate kinase and a dead-end combination of substrate and product: $\text{M(II)ADP} \rightleftharpoons 3\text{-phosphoglycerate}$. The apparent dissociation constant for vanadate from this complex is 0.1 mM (6). EPR measurements show that addition of vanadate to the dead-end complex with Mn(II) changes the symmetry of the zero-field splitting tensor of Mn(II) from axial to rhombic, and the magnitude of the change indicates that a ligand exchange has occurred in the primary coordination sphere of the metal ion (6). EPR measurements with $[\alpha\text{-}^{17}\text{O}]\text{ADP}$ and $\beta\text{-}^{17}\text{O}]\text{ADP}$ show that ADP is bound to Mn(II) as an α,β -bidentate complex before and after addition of vanadate. The geometry and position of vanadate in this complex is of considerable value in determining the structural basis for the potent inhibitory properties of vanadate.

The aim of this project is to determine the distance between the metal activator and Vanadium (as the vanadate anion) at the active site of the enzyme. If vanadate substitutes for the transferable phospho group, the Vanadium nucleus and the metal ion will be second-sphere neighbors. The EXAFS-spectra of Mn and of Vanadium will be used to determine the Mn-V distance.

So far the EXAFS-spectra of MnEDTA (whose 3-D crystal structure is known (7)), MnATP , MnADP and V_2O_5 have been recorded and will be used as reference. The data of MnATP and MnADP show structure beyond the nearest neighbor shell demonstrating that it might be possible to determine the Mn-V distance which is estimated to be 3.5 - 4Å.

EXAFS-data of MnATP at a concentration to which the protein can be readily concentrated (5 mM) showed that a sufficiently large S/N-ratio can be achieved.

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This work has been carried out on Beam Line X9-A: The National Biostructures PRT is supported by NIH through the Biotechnology Resource Program of the Division of Research Resources under Grant RR-01633 and NSF under Grant DMR-8519059.

PRECISION SUPPORT FRAME FOR FOUR-CIRCLE DIFFRACTOMETER ON BEAM LINE X9-A

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A support and transport frame for the Four-Circle Diffractometer has been constructed. This allows one person to move the diffractometer in and out of the hutch (experimental area) and to position it precisely into the x-ray beam.

Vertical positioning of the 1000 lb diffractometer is via four coupled lead screws driven by a remotely controlled DC-motor. An encoder is used for feedback. Positioning accuracies of a few micrometers have been achieved.

During horizontal position and angle adjustment, the whole assembly is riding on four air bearings allowing smooth adjustment. Two remote-controlled positioning stages with a resolution of a few micrometers are used to control the position and angle of the diffractometer with respect to the beam in the horizontal plane.

The frame is also equipped with a w inch which will counter-balance heavy weight detectors mounted on the 2 m long two-theta arm of the diffractometer.

Four-Circle Diffractometer with 2 m-long Two-Theta Arm in Experimental Hutch

This work has been supported by NIH under Grants RR-01633 (National Biostructures PRT) and GM-32692; and NSF under Grant DMR-8519059.

FEASIBILITY OF DIFFRACTION FROM THIN MUSCLE SPECIMEN WITH THE LINE FOCUSED BEAM

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The equatorial and meridional small angle diffraction patterns of thin sheets of smooth muscle (taenia coli and portal vein, 0.15 mm thick) have been recorded using the line focused beam produced by the vertically deflecting mirror.

Smooth muscle has weak diffraction peaks on a high background. Using conventional Cu-radiation, the peaks are close to the center on a steep slope, are not well resolved and require exposure times of 3-5 hours even with a rotating anode x-ray tube and a point-focusing optic (1).

The aim of this study was threefold: (i) to see if the 115Å equatorial reflection can be resolved from the background (ii) to measure the intensity of the reflection in order to predict the intensity with a point focused beam, and (iii) to find out if using a longer wavelength gives better results.

The diffraction patterns have been recorded with a linear position sensitive detector (courtesy of Dr. J.K. Blasie) with 3 mm slit height using both 1.74Å and 3.1Å radiation. With 3.1Å radiation, the patterns showed better resolved equatorial (Fig. 1) and meridional peaks at 115Å and 145Å than patterns recorded with 1.74Å radiation (Fig. 2). With 1.74Å radiation, the flux in both peaks (background subtracted) was about 10^3 photons/sec at 100 mA beam current. With the point focused beam, we expect a 10 x higher flux into the peaks thus making possible recording times of a second or less.

Fig. 1: Equatorial x-ray diffraction pattern from a thin sheet of smooth muscle (portal vein, appr. 0.15 mm thick)

Photon energy = 7.11 KeV (1.74Å); exposure: 21 min at 48 mA beam current; an Al-filter with a transmission of 0.098 has been used to prevent saturation of the PSD

(a) raw data, x-axis = detector channels

(b) x-axis converted into q-values ($q = 2\sin\theta/\lambda$)

(c) background subtracted

Fig. 2: Same as Fig. 1, but photon energy = 4.00 KeV (3.10Å); exposure: 13 min at 72 mA beam current; no filter

(a),(b) and (c) same as in Fig. 1

Note that the strong scattering close to the beam center has about the same width in real space but not in q-space. It is, therefore, a background from the instrument and not scattering of the specimen.

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This work has been carried out on Beam Line X9-A: The National Biostructures PRT is supported by NIH through the Biotechnology Resource Program of the Division of Research Resources under Grant RR-01633 and NSF under Grant DMR-85100050.

DEVELOPMENT OF A FLOW FLASH APPARATUS FOR X-RAY ABSORPTION STUDIES OF CARBOXY HEMOGLOBIN PHOTOLYSIS

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The flow flash apparatus, which was designed for the time resolved X-ray absorption studies of the photoproducts of metalloproteins, was tested on National Biostructures PRT Beam Line X-9A.

The major components of this apparatus are xenon flash lamps, sample handling system and the equipments for x-ray absorption data collection. Figure 1 is a top view of the setup for the X-ray absorption data acquisition. The "dark" EXAFS, which denotes the EXAFS spectra collected with xenon lamps off, and the "light" EXAFS, which were collected during flashes of the xenon lamps, were acquired on a 19 mM carboxy hemoglobin sample at room temperature from both the front and back side of the sample cells by means of plastic scintillation-PMT detectors. The detectors were in current integration mode and the fluorescence X-ray signals from the "light" and "dark" EXAFS were stored in separate channels by means of a dual signal switcher. The 8 millisecond duration of xenon light flash and 2 Hz repetition rate gave a duty ratio of 60 to 1 between the "dark" and "light" channels.

FIG. 1. FLOW FLASH APPARATUS FOR ROOM TEMPERATURE X-RAY ABSORPTION STUDIES OF HEMOGLOBIN-CO PHOTOLYSIS

The "light" and "dark" spectra were further processed by the conventional EXAFS data reduction procedure. Figure 2 shows a "light" spectrum (A) which is an average of twelve 0.16s/pt scans and a "dark" spectrum (B), which is an average of 12 corresponding scans. The signal-to-noise ratio for this "light" EXAFS is approximately 200 or 40000 effective photons per second based on the comparison of this "light" spectrum with an EXAFS scan of 5 mM myoglobin at 2 s/pt using fluorescence ionization chamber as detector. A "MATCH" program was employed from -45 to 200 eV relative to the midpoint of the absorption edge so that the "light" and "dark" spectra could be compared. These two spectra are almost identical if judged by eyes, as shown in Figure 3, where the solid line is the "dark" spectrum while the dashed line is the "light"

one. The deviation between these two spectra forms a Gaussian-shaped distribution which gives rise to a standard deviation of 7.4×10^{-3} relative to the edge jump. In another words, no structural difference between the "light" and "dark" carboxy hemoglobin can be detected by EXAFS. This indicates the relaxation of quaternary structure does not significantly affect the heme environment in carboxy hemoglobin. Further improvement of this apparatus is under consideration.

In conclusion, this flow flash apparatus has shown the potential for the EXAFS structural studies of room temperature time-resolved photolysis of biological materials.

FIGURE 2. AVERAGED "LIGHT" AND "DARK" SPECTRA OF HbCO USING THE FLOW FLASH APPARATUS

Dual Signal Switch, 2 flashes/s, 0.008 s/flash
Fe K-Edge, 126 pt/scan, 10 s/pt
A. Average of 12 "light" scans
B. Average of 12 "dark" scans

FIGURE 3. MATCH BETWEEN THE "LIGHT" AND "DARK" SPECTRA

Solid line: the normalized "dark" spectrum
Dashed line: the normalized "light" spectrum

Beam Line X9-A: Supported by NIH Grant RR-01633, and this work was supported by Grants GM-31992 and HL-18708.

MICROTOMOGRAPHY AT X-10

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We have developed the capability to image the 3-D structure of small (0.5-1.0 mm) samples. It is based upon the X-ray tomography technique, which uses the measurement of the attenuation of an X-ray beam by a material to mathematically reconstruct the interior features of the material. Our capability is unique because of the three-dimensional nature of the data obtained; we refer to it as 3-D Microtomography.¹ Typical microtomography techniques have involved the use of either a pinhole aperture for the definition of the incident and transmitted beams,² or a linear diode array to detect the transmitted beam.³ Our technique improves on both of these.

The detector used for these measurements is a novel, imaging area detector developed at EXXON. It allows for the simultaneous acquisition of approximately 300 projection measurements through the sample, thus giving 300 stacked planes in the reconstructed image. This compares with the single plane obtained for the conventional medical CAT scan, as well as for the two microtomography techniques mentioned. With the use of a graphics capability, our technique allows the viewing of the complete 3-D structure of the sample.

An additional improvement over previous microtomography experiments has been made in spatial resolution. Systems which have employed a fixed aperture to perform the beam definition have been limited to approximately 5 micro resolution. Diode arrays have a pixel size of approximately 25 microns. Our system is currently capable of about 1.0 micron resolution for a reconstructed image. Both of these figures can be improved, and efforts to do so are in progress.

Samples studied have included a variety of heterogeneous materials with both density and chemical variations. Since the technique does not uniquely distinguish between density and chemical differences in a single measurement, the ability to use two energies in two scans of a sample is important. By tuning the X-ray energy it is possible to distinguish between these two effects and thus to quantitatively determine the chemical/density composition of the sample. We have successfully done this to determine the transition metal content in chemically heterogeneous samples.

Plans for the future include the construction of a dedicated tomography facility. We have been given approval by the NSLS to build a beamline which will be optimized for performing X-ray microtomography. The beamline will be constructed so as to allow photon energy, band pass, and beam size to each be varied over a wide range. This will permit a wider variety of samples to be routinely studied.

We will also attempt higher resolution studies, as well as studies of dynamic processes such as flow behavior. Both of these will entail improvements on the existing system, but represent direct and tractable extensions of proven capabilities.

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X-RAY STUDY OF THE STRUCTURE OF $\text{Pb-}c(5\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ OVERLAYER ON $\text{Cu}(100)$ SURFACE

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The study of structures and structural behaviors of metal overlayers is very relevant to many areas of research such as epitaxial growth, surface modification, and catalysis. Such a study has been performed recently on EXXON beamline (X10A) on $\text{Pb-}c(5\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ overlayer on $\text{Cu}(100)$ surface. We studied the structure and the melting behavior of this overlayer using grazing incidence x-ray diffraction technique.

The $c(n\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ structures with centered rectangular unit cells are commonly observed on many metal overlayer systems on surfaces with four-fold symmetry. Previous LEED studies of Pb on $\text{Cu}(100)$ showed a series of ordered structures at increased coverages.¹⁻² The $c(5\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ structure is formed at about 0.6 monolayer. Using the highly focused source from our beamline, x-ray measurements of this Pb overlayer revealed not only the superlattice reflections associated with the (5×1) modulation but also additional satellites (Fig. 1a). The integrated intensity observed at the strongest reflection at $(1.2, 0)$ from the Pb overlayer was over 10^4 c/s.

Structural analysis has been performed on the basis of the 20 fractional-order superlattice reflections measured.³ The Patterson map gives a 6-atom unit cell with an antiphase-type atomic arrangement in the cell. The result is qualitatively similar to that proposed by a recent LEED study.² However, the satellite reflections, as observed with Q vector nearly normal to the superlattice modulation, suggests the presence of coherent domain walls. Based on this x-ray study, a tentative picture of the overlayer structure is proposed, as shown in Fig. 1b.

Fig. 1 (a) Part of the superlattice and satellite reflections measured on $\text{Pb-}c(5\sqrt{2} \times \sqrt{2})\text{R}45^\circ/\text{Cu}(001)$ surface. Axes in units of $2\pi/3.615\text{\AA}^{-1}$. $a_s \times b_s$ represent the surface unit cell. Filled squares: bulk forbidden reflection, circles: superlattice reflections, crosses: satellite. Pb coverage corresponds to an Auger ratio of 0.44 of $\text{Pb}(93\text{ eV})/\text{Cu}(60\text{ eV})$. The reflections from an equivalent domain rotated by 90° are not shown.

(b) A schematic of the proposed structure of $\text{Pb-}c(5\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ on $\text{Cu}(100)$ surface. Small circles: Cu, large circles: Pb, shaded area: domain walls. Note the antiphase-type atomic arrangement in the 6-atom unit cell and the presence of the domain walls.

Preliminary study of the melting behaviors of this Pb overlayer was also performed. We observed large changes of the intensities of both superlattice and satellite reflections before melting of the overlayer at $\approx 220^\circ\text{C}$. This indicates that the domain walls probably play an important role in the melting. To understand the nature of the melting of this Pb overlayer will be a subject for our future study.

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THE STEP ROUGHENING TRANSITION OF A Cu(113) SURFACE STUDIED BY SURFACE X-RAY SCATTERING

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Since the first demonstration of monolayer sensitivity of x-ray diffraction from the surface, the grazing incidence x-ray scattering (GIXS) technique is quickly emerging as an important structural probe for surface and interface studies.¹ On EXXON beamline (X10A), GIXS work has been performed using a z-axis type surface scattering spectrometer with integrated UHV and surface preparation capabilities. In this report, we discuss the results of a GIXS study on a stepped surface, Cu(113), and the observed roughening transition on this surface.

The equilibrium roughening of a stepped surface can be described in terms of thermally created atomic steps and kinks.² Experimentally, the thermal roughening ("meandering") of the lines of steps on surfaces at elevated temperatures has been observed in the He atom diffraction experiments on vicinal surfaces of Cu and Ni,³ but the interpretation of the results is complicated due to multiple and inelastic scattering.

A typical x-ray in-plane scan is shown in Fig. 1a, which was measured in the direction normal to the steps on a Cu(113) surface quenched from high temperature. We notice that the peak at wave-vector transfer $Q=1$ (in unit of $2\pi/4.239\text{\AA}^{-1}$, corresponding to the step-step distance of $4.24\text{\AA}$) originates from ordered steps and the satellites at $Q=0.85$ and 1.15 . Such a step superlattice peak was observed only after rigorous surface cleaning and annealing cycles. The width of the peak corresponds to a coherence length of $\sim 170\text{\AA}$. The satellite peaks were not observed when the sample was slowly cooled from high temperature, indicating that such a structural modulation is only metastable.

Fig. 1 (a) An in-plane longitudinal scan on a Cu(113) surface quenched from 710°C . One notes that the step superlattice peak at $Q=1$, originating from the ordered steps, is accompanied by satellites.

(b) The integrated intensity of the step superlattice peak as function of temperature.

Squares were taken on heating and triangles on cooling. The solid line is a fit to a form derived from Ref. 2.

The reversible step roughening transition was observed when x-ray measurements were done by slow cooling. The integrated intensity of the step superlattice peak as a function of temperature obtained under such conditions is shown in Fig. 1b. By fitting the intensity curve so measured, we can compare our results with the theory of the step roughening given by Villain, et al.³ From the analysis we obtain for Cu(113) surface, a kink energy of $2100 \pm 75\text{ K}$ and a step-step repulsion energy $86 \pm 10\text{ K}$, with a roughening transition temperature of $620 \pm 10\text{ K}$. We note that the surface steps become "rough" at relatively low temperature with respect to the bulk melting temperature of Cu ($T_m = 1356\text{ K}$).

In short, we have demonstrated that ordered surface steps can be observed using surface x-ray scattering. The results on Cu(113) surface show directly the roughening transition.

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X-RAY ABSORPTION STUDIES AT THE M-EDGE OF URANIUM AND NEPTUNIUM COMPOUNDS

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A systematic study has been undertaken at the M absorption edges of a series of Uranium and Neptunium compounds with +3, +4, and +5 valencies for U, and with +3, +4, +5, and +7 valencies for Np, to establish the M-edge XANES spectroscopy as an effective probe of unoccupied valence electronic states. The M_V and M_{IV} edges correspond to 3d to 5f transitions, while M_{II} and M_{III} correspond to 3p to 6d, and M_I correspond to 3s to 7p transitions. As a result, by complete analyses, one can probe the entire unoccupied valence electron bands. In the case of U intermetallic compounds, the main interest is in 5f electrons which are in an intermediate regime where the 5f electron-electron correlation energy is comparable to 5f bandwidth. This makes it possible to synthesize intermetallic systems with varying degrees of localization of 5f bands with proper doping. We have looked into compounds like URh_3B_x ($0 < x < 0.8$), $URh_{3-x}Pd_x$ ($0 < x < 2.0$), and $UIr_{3-x}Pt_x$ ($0.4 < x < 2.6$), in which the electronic character changes from localized to itinerant in each series. These samples were already characterized by electrical resistance, magnetic susceptibility, specific heat (1), and by X-Ray Photoemission Spectroscopy (2). For standard compounds, like UO_2 and UCl_4 , relativistic first principal self-consistent molecular cluster calculations have been made to aid the interpretation of distinct features in the spectra. Similarly, M-edges of a series of Np compounds, like NpP , $NpRu_2$, $NpSn_3$, and Np-metal have been measured. The degree of itineracy in these compounds is known to change from Mössbauer Spectroscopy measurements (3). A new data analysis package has been developed to normalize the spectra for proper comparison. The existing procedure of passing a polynomial spline through the smoothly varying background to obtain a normalized step jump across the absorption edge did not give reproducible results.

Fig.1 U M_V -edge corresponding to 3d_{3/2} to 5f transitions.

Fig.2 U M_{III} -edge corresponding to 3p_{3/2} to 6d transitions.

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(*) Work supported by US DOE, BES-Materials and Chemical Sciences, under contract #W-31-109-ENG-38

EXAFS STUDIES OF BURIED INTERFACES: Al on GaAs

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When x-rays undergo total external reflection from an interface, the x-ray beam penetrates the sample only a few tens of Angstroms. By combining this with x-ray fluorescence detection, EXAFS studies with high surface sensitivity are possible. Further, if a low-density material overlies a higher-density substrate, it is possible to tune the angle of incidence to penetrate the overlayer and reflect from the buried interface.

An example of how this technique could be applied is to study metallization of semiconductor surfaces (e.g. Al on GaAs) and directly determine interdiffusion, compound formation, and phase segregation near the interface. Measurements of Al on GaAs have been undertaken to study the feasibility of this technique. The experimental configuration is shown in Fig. 1. The two samples were MBE-grown GaAs with 500Å of Al deposited *in situ* at (a) ambient growth temperature, approximately 500C, and (b) 90C. Our preliminary results show clear interdiffusion of Al into the GaAs, especially for the sample deposited at high temperature. Figure 2 shows EXAFS oscillations of for the two samples.

An important advantage of the buried-interface work is that we may study samples that have been prepared and well-characterized earlier. The measurements may also be made in open air, which significantly simplifies the experiment.

Fig. 1. Experimental configuration for the EXAFS study of buried interfaces.

Fig. 2. As-edge EXAFS oscillations for 500Å of Al on GaAs, for samples prepared at (a) 500C, and (b) 90C.

EXAFS STUDY OF TRANSITION METAL ENVIRONMENTS IN SILICON SYSTEMS

PREPARED BY HIGH DOSE ION IMPLANTATION

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Recent studies¹ have shown that high dose ion implantation of transition metals into single crystal silicon at elevated temperature (e.g. 350°C) leads to silicide thin film formation at the surface. Implantation at room temperature followed by thermal annealing also leads to the formation of silicides. Such thin film silicide systems are considered to be of great importance in VLSI technology. The compound formation mechanisms and their dependence on thermodynamics and kinetics are also of interest.

The EXAFS technique is well suited to study the local transition metal atom environment in these implanted systems, and the compound formation sequence. The information on atomic bonding obtained from an EXAFS study may be helpful to the understanding of the silicide formation mechanism. We initiated such studies on cobalt and nickel implanted into Si(100) wafers at an energy of 150 keV and dose rate of 10-15 A/cm². Three samples were studied, samples A: Co-Si, wafer temperature T = 100°C, Dose = 7.5 x 10¹⁷ Co⁺/cm²; Sample B: Co-Si, T = 350°C, Dose 8.0 x 10¹⁷ Co⁺/cm²; Sample C: Ni-Si, T = 350°C, Dose = 8.0 x 10¹⁷ Ni⁺/cm². The EXAFS measurements were performed at beam line X-11, using a 45°-45° fluorescence detection method at near liquid nitrogen temperature (NT). The X-ray polarization forms a 45° angle with the sample surface normal.

The Co K-edge EXAFS of samples A and Sample B are similar. The Fourier transform magnitude of a k³ weighted EXAFS for Sample A is shown for Fig. 1 with the backscattering atoms indicated at the corresponding peaks. Least square curve fitting using theoretical backscattering amplitude and phase² was employed to extract the structural parameters including coordination number N, bond length R and mean square relative displacement σ^2 about the Co atom. A typical fit is presented in Fig. 2. We combined the log ratio method and curve fitting to minimize the effect of correlations among N, σ^2 and E₀, and correlation between R and E₀. We estimate the uncertainty of N and σ^2 to be 15%, and $\Delta R = 0.03 \text{ \AA}$. Details of data analysis will appear elsewhere. Table 1 lists the results of fitting for sample A and B. For Sample C; large Bragg peaks made data analysis hard to proceed on the existing spectra. A rotating sample stage will be used for the future studies.

The Neff is the effective coordination number in EXAFS, it represents the real coordination number for nearest neighbor only if the sample is isotropic which is not the case for the samples under study.

Since the near neighbor distances are determined up to 4.0 Å, a comparison with the known neighbor distances of CoSi, Co₂Si and CoSi₂ suggests that the phase in Sample A and B is dominantly (if not all) CoSi of cubic FeSi₃ type structure. Comparison of fitted N, R with the value of CoSi (calculated from known structure³) in table 1 leads us to conclude that the silicide in both Sample A and B are highly oriented with respect to the surface, and might be single crystal. The rather peculiar behavior of Neff is due to the orientation and polarization of the X-rays. The orientations of CoSi in Sample A and B are different. Further EXAFS measurement should help to determine the precise orientation of the silicide by changing the sample orientation with respect to X-ray polarization, X-ray diffraction will also be utilized for such purpose. The complete suppression of the Si shell at 2.47 Å might be due to the orientation of the CoSi, but we should not exclude the possibility that these bonds are contracted to ~2.3 Å such that EXAFS sees only a single shell at 2.31 Å. This will be clarified by further EXAFS experiments. In fact, X-ray diffraction on Sample B annealed at 750°C for 1 hour showed a large line from Co Si (311) plane and two other much weaker lines. The latest work⁴ shows that nearly single crystal CoSi₂ can be formed by Co⁺ implantation at dose as low as 2.5 x 10¹⁷ Co⁺/cm² without post annealing.

A large σ^2 for Co-Co at R = 4.0 Å versus a small σ^2 at R = 2.7 Å suggests that the vibrations of nearest Co neighbors are highly correlated, since it is reasonable to believe that the far separated atom pair is less correlated. Such a small σ^2 at R = 2.7 Å indicates further that the nearest Co-Co atom pair tends to vibrate in phase.

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Acknowledgement

This work was performed at Beam Line X-11 at the NSLS and is supported by the Division of Materials Science of DOE under contract No DE-AS05-80-ER10742.

Fig. 1. Transform magnitude of $k^3 \chi$, Co K-edge fluorescence at NT of Co-Si ($E=150$ keV, $T=100^\circ\text{C}$, Dose 7.5×10^{17} Co $^{+}$ /cm 2). The window for inverse transform is also shown.

Fig. 2. Inverse transform $k^3 \chi$ from Fig. 1 (line) and fit (dots). R: 1.0-3.0 Å.

Table 1. Structural parameters obtained by fitting the Co K-edge EXAFS spectra at liquid nitrogen temperature. Sample A: Co $^{+}$ $\rightarrow$ Si (100), $E=150$ keV, $T=100^\circ\text{C}$, dose = 7.5×10^{17} Co $^{+}$ /cm 2 ; Sample B: Co $^{+}$ $\rightarrow$ Si (100), $E=150$ keV, $T=350^\circ\text{C}$, dose = 8.0×10^{17} Co $^{+}$ /cm 2 .

Sample A					Sample B					CoSi (RT)		
$N_{\text{eff}}^{(a)}$	type	R	σ^2	E_0	N_{eff}	type	R	σ^2	E_0	N	type	R
		(Å)	(10^{-3}Å^2)	(eV)			(Å)	(10^{-3}Å^2)	(eV)			(Å)
5.1	Si	2.31	7.5	-10.3	6.6	Si	2.31	9.6	-9.3	1	Si	2.287
										3	Si	2.331
										3	Si	2.471
2.3	Co	2.71	1.7	-10.1	2.3	Co	2.71	0.4	-10.1	6	Co	2.729
$^{(b)}$	Si	3.60	*	*	*	Si	3.55	*	*	3	Si	3.641
4.8	Co	4.00	6.7	-8.3	6.8	Co	4.04	8.0	-10.8	6	Co	4.019

(a) A scaling factor of $S_0^2 = 0.70$ was used for Co absorber.

(b) Reliable value not available for these parameters.

X-RAY ABSORPTION STUDIES OF Cr OXIDE/SiO₂ OLEFIN POLYMERIZATION CATALYSTS

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The oxidation state and local geometry of chromium on CrO_x/SiO₂ catalysts and their synthetic intermediates was studied using x-ray absorption spectroscopy. These catalysts, which are used commercially for olefin polymerization, typically contain about 0.2 wt% Cr. Analysis of the chromium K absorption edges provided much information on the stepwise changes in the metal oxidation state during catalyst preparation. In-situ exposure of the catalyst precursor to actual polymerization conditions enabled determination of final average chromium oxidation state of the activated catalyst. The effect of titanium modifiers on the Cr active site was also investigated.

The as-received catalyst contains Cr in a mixture of primarily +3 and +6 oxidation states. (The presence of Cr+6 is primarily monitored by the intensity of the pre-edge absorption arising from a formally forbidden 1s→3d transition.) Activation of the as-received catalyst oxidizes all of the Cr to +6. A number of different catalysts modifiers, added to primarily control polymer product properties, cause reduction of a significant fraction of Cr, mostly to the +3 oxidation state. After initial polymerization reactions begin, the Cr is almost exclusively in an average oxidation state of +3. Catalyst modifiers and initial polymerization, unlike the results found for Cr, have little if any effect on Ti oxidation state. Ti remains in the +4 state in all samples examined.

*This work was performed on beamline X-11A at the NSLS and is supported by the Division of Materials Science of DOE under Contract No. DE-AS05-80-ER10742.

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Glancing angle reflectivity and EXAFS techniques provide the possibility of probing interfacial atomic structures without damaging samples. To demonstrate their sensitivity to interfaces, we have compared samples composed of 1000-Angstrom-Al/1000-Angstrom-Cu/glass prepared by evaporation and sputtering. Previous studies found differences between the two interfaces (H. Chen et al. 273, NSLS Annual Report, 1986). Intermixing was observed at the sputtered interface. This work follows the development of CuAl_2 layer at both interfaces upon annealing. Each sample was annealed at temperatures ranging from 100°C to 200°C for 5 minutes at each step. Short annealing times were used so that the compound would not be too thick and the initial stages of compound formation could be studied.

The reflectivity as a function of x-ray incident angle probes the macroscopic structure of thin films, e.g. thicknesses and roughnesses. A growth of an interface layer causes changes in the reflected signal. Figure 1 shows the reflectivity data taken from the two samples as deposited and after the final stage of annealing, 5 minutes at 200°C. One can notice the reduction of amplitudes on the evaporated one (curve Ea2, Eb2). More drastic change can be seen in the sputtered case (curve Sa2, Sb2). An extra peak shows up clearly in Sb2. It is believed to be the reflection from the new CuAl_2 layer.

By choosing a reasonable incident angle, one can look at the atomic environment at a certain depth by collecting fluorescent signals, from which EXAFS can be extracted. EXAFS is very sensitive to neighboring atom species and interatomic distances. Therefore it is able to show whether the signal is from pure Cu or from a Cu-Al mixture. In Fig. 2 EXAFS from the two samples are compared to the standards, namely Cu and CuAl_2 . Despite minor differences, the two annealed ones (third curves from top) have the main feature of CuAl_2 . It means that although the macroscopic qualities of the two films are different (which caused the difference in the reflectivities), the microscopic picture is probably very similar.

Difficulties were encountered when further analysis was attempted. Quantitative results can be obtained only when the distortion problem is solved. Corrections have been made on pure Au thin film data and were quite successful.¹ Further efforts are needed for bilayer situations.

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Acknowledgements

This work was performed at Beam Line X-11, NSLS and is supported in part by U.S. Department of Energy, under Contract Nos. DE-AS05-80-ER10742 and DE-AC02-76CH00016.

Fig. 1 Reflectivity data below and above the absorption edge of Cu from sputtered samples and evaporated samples, as deposited and annealed at 200°C for 5 minutes, respectively.

Fig. 2 EXAFS data taken at an incident angle around 4.5 Mrad from sputtered samples and evaporated samples, as deposited and annealed at 200°C for 5 minutes, respectively.

STRUCTURE OF RHODIUM/CERIUM γ - Al_2O_3 CATALYST WITH EXAFS

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INTRODUCTION

Noble metal catalysts dispersed on metal oxides are essential in meeting automotive emission standards. In particular, Rh is essential in these catalysts¹. Rhodium catalysts are durable under normal operating conditions but extended exposures to high temperature results in the loss of catalytic activity. The incorporation of Ce in the support permits the sample to maintain stoichiometry during brief excursions into reducing environments. Changes in Rh and Ce structure and chemistry accompanying oxidation, reduction or deactivation are of interest. A number of previous studies² on supported catalyst have demonstrated the capability of EXAFS to address these interests.

RESULTS

A 0.5 wt% Rh, 5 wt% Ce, γ - Al_2O_3 catalyst was treated at 1173°K in flowing 5% O_2/N_2 . A second pellet was treated at the same temperature in 5% H_2/N_2 . The samples were cooled to room temperature and then stored in air until the x-ray absorption measurements were made of the Rh K-edge and Ce L_{III} -edge. The k^2 weighted Fourier transforms of the Rh K-edge of the reduced catalyst are shown in Fig. 1. The oxidized catalyst shows no evidence of Rh-Rh coordination. The Rh atoms are completely dispersed with only anion near neighbors. In contrast, standard analysis techniques³ show the reduced catalyst contains small Rh particles which have a Rh-Rh coordination of ≈ 4.1 at the bulk spacing. The persistence of this reduced state despite exposure to air is surprising.

Fig. 1 Rh K-edge Fourier transforms.

Fig. 2 Ce L_{III} -edge XANES.

The L_{III} near edge structure of the oxidized and reduced catalyst were least squares fit to a weighted sum of the CeO_2 , $\text{Ce}(+4)$, and cerrous acetate, $\text{Ce}(+3)$ edges. The results, shown in Fig. 2, demonstrate that there is an appreciable change in the valence of Ce between oxidizing and reducing conditions. After normalizing the edge jumps to unity, the resulting fit for the reduced catalyst (X) gives $0.50\text{Ce}(+4) + 0.50\text{Ce}(+3)$, while for the oxidized catalyst (Δ) the result is $0.94\text{Ce}(+4) + 0.06\text{Ce}(+3)$. This supports the view of cerium's role as an oxygen reservoir which can buffer excursions into reducing conditions.

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This work was supported in part by the General Motors Research Laboratories.

EXAFS MEASUREMENTS OF Ni(OH)_2 WITH COPRECIPITATED Co AND Fe

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INTRODUCTION

While previous EXAFS experiments have investigated the structure of pure nickel hydroxide¹, the structural information obtained here by EXAFS should provide a better understanding of how foreign ions such as Co and Fe have beneficial and detrimental effects, respectively, on the charge storage efficiency of nickel battery electrodes².

RESULTS

Coprecipitation of 10% Co into Ni(OH)_2 yielded a material with a Co K-edge EXAFS spectrum as shown in Fig. 1. Analysis results for this k^2 -weighted Fourier transform to obtain the coordination distances for the first two shells is summarized in Table I. The first coordination shell, thought to consist of 6 oxygen atoms, is contracted significantly in comparison to the Co-O shell of $\beta\text{-Co(OH)}_2$, indicating Co may be present in a higher oxidation state in the coprecipitated material. Further, the coordination distance of the second shell, thought to be 6 metal ions, is in close agreement with the Ni-Ni distance in Ni(OH)_2 , providing evidence that the oxidized Co ions are incorporated into the Ni lattice. Finally, a third peak centered at 3.6 Å in the Fourier transform may be indicative of the presence of Co sites in interlamellar octahedral holes in the brucite structure.

Fig. 1 Co K-edge Fourier transforms.

Table 1. Coordination Distances (Å)

coprecipitated Co/Ni hydroxide^a:

shell I (Co-O)	1.86
shell II (Co-M)	3.06

β -nickel hydroxide^b:

Ni-O	2.07
Ni-Ni	3.12

β -cobalt hydroxide^b:

Co-O	2.07
Co-Co	3.17

^aAnalyzed using $\beta\text{-Co(OH)}_2$ reference.

^bFrom reference 3.

Coprecipitation of 10% Fe into Ni(OH)_2 produced a material with a K-edge Fe EXAFS spectrum essentially identical to that of $\alpha\text{-FeOOH}$ which has a diascore structure. Analysis also yielded identical coordination distances, within statistical uncertainty, indicating the Fe/Ni coprecipitate may actually consist of a mixture of the Ni(OH)_2 and $\alpha\text{-FeOOH}$.

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This work was supported in part by NASA Grant NAG-3-894.

EXAFS OF AN ENZYME TRANSIENT: ESO₂ OF PROTOCATECHUATE 3,4-DIOXYGENASE (PCD)

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The iron-containing dioxygenase, PCD, catalyzes intradiol cleavage of catechol derivatives according to the minimal scheme:

where E = PCD, S = protocatechuate or dihydroxyphenylpropionate (DHPP) to yield a tricarboxylic acid. We have reported earlier on the EXAFS of E and ES, as well as enzyme-inhibitor complexes.¹ In the present study, the catalytically competent intermediate, ESO₂, was prepared by freeze-trapping at -80°C and its EXAFS measured.

To obtain sufficient ESO₂ (2 mM, 300 µl), the enzyme was presaturated with 3 atm. oxygen at 5°C. Addition of 30 µl of concentrated DHPP solution, rapid transfer to the EXAFS cell, followed by quick freezing provided the sample. Total elapsed time of preparation was 90 sec. and, thus, the technique is not a rapid freeze-quench process. The use of excess oxygen (ca. 10 mM) caused ESO₂ to be the majority species (99%) during the preparation and transfer. Sample integrity was verified by use of a double-beam fiber optic spectrometer.

After twelve hours of beam exposure, the optical spectrum had changed. This alteration was assigned to radiolytic products of oxygen in the mildly basic solution. That the iron-site was not altered due to beam exposure was demonstrated by warming the solution, allowing oxygen to be consumed, and observing that the ES species is formed.

Figure 1 displays transforms of E, ES, and ESO₂. The sharp peak at R = 2.5 Å is indicative of chelation by substrate in ES, and its absence in ESO₂ clearly establishes loss of such chelation. The peak at R = 3.8 Å is due to the presence of histidyl ligation. Likely structures of ESO₂ have been modeled using spherical wave calculation of single and multiple-scattering EXAFS contributions. Data excludes a pseudoanhydride or peroxo complex, but the ring-opened and product-like structures of Fig. 2 are compatible with the EXAFS result.

Fig. 1. Comparison of E, ES, and ESO₂

Fig. 2. Possible structures of ESO₂.

Supported by NIH GM23474

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It has been recognized for sometime that spherical wave theories of EXAFS are more accurate than those utilizing the planewave approximation. Recently, Rehr and co-workers,¹ employing a spherical wave (SW) theory, calculated Br_2 and Cu EXAFS, and earlier others²⁻⁴ have examined EXAFS (in distinction to XANES) of Cu, NiO, and $\text{Co}(\text{H}_2\text{O})_6$. We extend the calculations to other transition metal complexes, and additionally examine imidazole (Im) or catechol (Cat) complexes of Mn, Fe, Co, Ni, Cu, and Zn, in which multiple scattering is clearly observed. Calculations employ the muffin-tin model with a potential modified by the energy-dependent Dirac exchange. The mean-free path term includes the "universal" photoelectron lifetime corrected for the core-hole lifetime. The energy zero is found from calculation of $\Delta E = E(1s_{3d^n}) - E(1s_{3d^{n+1}})$ and the muffin-tin zero. In the instance of $\text{Ni}(\text{Im})_6$ a Debye-Waller factor is found from the temperature-dependent data. In other cases σ^2 is a parameter for the first-shell. Multiple-scattering calculations are limited to three atoms and near-forward scattering paths. A spherical wave approximation (SWA) is used for multiple-scattering, while the SW is exact for single-scattering.

Figure 1 displays data, and planewave and SW calculations for a single-shell example, $\text{Co}(\text{NH}_3)_6^{3+}$. The superiority of the SW calculation is due in large part to the modification of the back-scattering phase at low k . Examples of multishell calculations are shown in Figs. 2 and 3, in which an E_0 shift of 5 eV for the SWA contribution is necessary.

We conclude that the spherical wave computations are acceptable for $k > 3 \text{ \AA}^{-1}$, but are poor in the near edge regime. Extension of the calculations to biological systems is feasible and is in progress.

Fig. 2. $\text{Ni}(\text{Im})_6^{3+}$. Data (—), single-scattering SW (···), full calculation (---).

Supported by NIH GM23474.

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Fig. 1. $\text{Co}(\text{NH}_3)_6^{3+}$. Data (—), SW (---), PWA (···).

Fig. 3. $\text{Fe}(\text{cat})_3^{3-}$. Legends as in Fig. 2.

S. M. Heald and J. M. Tranquada (Brookhaven National Laboratory)

Superconductors with the composition $\text{La}_{2-x}(\text{Ba},\text{Sr})_x\text{CuO}_{4-y}$ and $X = 0.0$ to 0.3 have been studied through measurements of x-ray absorption near-edge structure at the Cu K and La L edges. Contrary to recent band structure calculations, we find that the Cu 3d electrons are localized with the copper ions having an integral $3d^9$ configuration ($2+$ valence) independent of dopant concentration (see Fig. 1). Variation in the area of the "white lines" at the La $L_{2,3}$ edges which increase with doping indicates that reduction of the valence charge results in an increase in unoccupied states (probably consisting of holes in the O 2p band) having d-symmetry relative to the La site. These O 2p holes also appear to have d-symmetry with respect to the Cu sites.

From measurements of extended x-ray absorption fine structure (EXAFS) at the Cu K edge between 10 and 300 K, we have also determined the temperature dependence of the mean square relative displacements σ^2 for Cu-O, Cu-La, and Cu-Cu near neighbors in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ with $X = 0, 0.15$, and 0.3 (see Fig. 2). It is found that σ^2 for Cu-O and Cu-La neighbors shows little variation with X . Model calculations have been used to demonstrate that $\sigma^2_{\text{Cu-O}}$ is sensitive to softening of the Cu-O breathing mode which has been predicted to be important for superconductivity in these materials. The Cu-O bonding is observed to be quite strong and no evidence is found for any significant change in the breathing mode frequency with doping.

Acknowledgements

This work was performed at Beamline X-11 at the National Synchrotron Light Source and is supported in part by the U.S. Department of Energy under Contract Nos. DE-AS0580-ER10742 and DE-AC02-76CH00016.

Fig. 1. Normalized XANES at the Cu K edge in $\text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_{4-y}$ as a function of doping.

Fig. 2. Temperature dependence of σ^2 for Cu-O, Cu-La and Cu-Cu shells in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$: circles, $X = 0$; squares, $X = 0.15$; triangles, $X = 0.3$.

S. M. Heald and J. M. Tranquada (Brookhaven National Laboratory)

EXAFS techniques have been shown to be valuable in studying multilayer structure, particularly in identifying and quantifying interface phases¹. In this work it is shown how standing wave effects can be used to permit EXAFS measurements to probe structure within the multilayer unit cell. When the multilayer is set to Bragg reflect x-rays, standing wave fields are set up which modulate the electric field intensity within the multilayer period. By controlling the angle it is possible to control the phase of the standing wave, and the region within the multilayer contributing most strongly to the x-ray absorption. EXAFS measurements can then probe the local structure in this region. A complication arises from the energy scans necessary for EXAFS measurements. Changing the energy necessitates an angle change in order to maintain a fixed standing wave configuration. This is accomplished by using a precision angle stage capable of 0.3 arcsecond steps.

Measurements were made on a Ni-Ti multilayer under study for neutron optics applications. Figure 1 shows the Fourier transforms of the Ni K-edge EXAFS for the multilayer compared to bulk Ni. The signals are quite similar in shape with the amplitude for the multilayer case showing a significant reduction and a strong angle dependence. In Fig. 2 the first shell EXAFS amplitude is plotted as a function of angle and shows a strong modulation near the multilayer Bragg peak at 8.23 mrad. The amplitude reduction comes from the fact that the measurements were made using fluorescence detection and the Ni concentration is high. As the standing wave field is set up the Ni contribution to the absorption is modulated, changing the amplitude reduction. A calculation of this effect assuming an ideal multilayer gave the solid line in Fig. 2. Considering that the calculation had no adjustable parameters and ignored anomalous dispersion effects, the agreement is quite good, and clearly verifies the standing wave modulations.

For the Ni layers there is little difference from bulk Ni indicating little intermixing with Ti. The Ti EXAFS, however, indicated the presence of significant low-z contamination determined to be C and O impurities. These were undoubtedly picked up during deposition and standing wave analysis found them to be uniformly distributed throughout the Ti layer. Including these impurities in the calculation in Fig. 2 gave the dashed curve which agrees slightly better with the measurements.

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We thank A. Saxena for providing the sample. This work was performed on Beamline X-11 at the National Synchrotron Light Source and is supported by the U.S. Department of Energy under Contract Nos. DE-AS05-80-ER10742 and DE-AC02-76CH00016.

Fig. 1. Fourier transform of the Ni EXAFS for the multilayer at 8.02 mrad (solid line) and 9.41 mrad (dashed line) compared to pure Ni. The scale for the multilayer is on the left and for the foil on the right.

Fig. 2. Reduction in the EXAFS amplitude for the Ni first neighbor shell. The points are the data and the solid curve the calculated reduction factor for an ideal multilayer. The dashed curve includes the effect of the O and C impurities observed by EXAFS.

THE INHIBITION OF CORROSION OF ALUMINUM BY CHROMATE USING FLUORESCENCE DETECTION OF SURFACE X-RAY ABSORPTION

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Chromate species are efficient inhibitors of the corrosion of aluminum in neutral aqueous environments, although the precise mechanism is far from clear. Presently, mechanisms include: (1) The reduction of Cr^{6+} or Cr^{3+} species, developing solid, hydrated Cr_2O_3 . The location of Cr_2O_3 is the subject of discussion, thought to develop generally over the alumina film surface^{1,2} or locally at flaws within the alumina film³. (2) The gradual penetration of Cr^{6+} species through the outer alumina film regions. (3) The catalysis of $\text{Al}(\text{OH})_3$ precipitation at anodic sites.

Analysis of aluminum specimens was carried out using x-ray adsorption by fluorescence detection, with incident x-rays at a glancing angle to the specimen⁴. Shifts in the adsorption edge or changes in the preedge structure occurred with changes in valency, allowed determination of species. Two standards (K_2CrO_4 and Cr_2O_3) were analyzed using transmission x-ray absorption to characterize the Cr VI and Cr III states. Superpure aluminum (99.99%) specimens were electropolished; barrier-type anodic films were formed by anodizing to selected voltages in borate electrolyte. The specimens were then immersed under open circuit conditions for one hour in a 1mM NaCl, 2mM K_2CrO_4 (pH 8) electrolyte.

Analysis of the K_2CrO_4 standard showed a large pre-edge peak at the K adsorption edge. This was not observed for the Cr_2O_3 standard and, allowed ready differentiation between the Cr VI and Cr III states (Figs. 1 and 2). Comparison of the height of the pre-edge peak to the edge height were closely related to the ratio of Cr VI to Cr III present. After immersion, aluminum bearing the air-formed film ~2 nm thick) showed no pre-edge peak, indicating chromium was present predominantly as Cr III. This was reinforced by an edge position close to that of the Cr_2O_3 standard (Fig. 1). Aluminum, supporting anodic films (e.g. 36 nm), showed a strong pre-edge peak and an edge position corresponding to that of the Cr VI standard, indicating that chromium was present primarily as Cr VI. An intermediate situation was apparent for a specimen carrying an anodic film, which has been formed to a thickness of 6 nm. Here the pre-edge peak was less strong and the edge itself shifted towards the Cr III edge position, revealing that both Cr III and Cr VI were present (Fig. 2). Previous work has shown a declining population density of persistent flaws with increasing thickness of barrier anodic films³. Thus, less Cr III should be detected on specimens bearing thicker films if reduction of Cr VI and Cr III is occurring within flaws. Thus, the results indicate that film thickening by anodizing corresponds to reduced detection of Cr III when the specimens are examined after immersion in a chromate containing electrolytes.

Acknowledgements

This work was supported by the U.S. Department of Energy, Divisions of Materials Sciences and Chemical Sciences under Contract Nos. DE-AC02-76CH00016 and DE-AS05-80-ER/0742. The authors would also like to thank the Science and Engineering Research Council for financial support to J. Hawkins.

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Fig. 1. Comparison of the absorption edges for chromium in the Cr_2O_3 standard with an air formed film after immersion for 1 h.

Fig. 2. Comparison of the absorption edge for chromium in the K_2CrO_4 standard with a 5V anodic film after immersion for 1 h.

In this study, EXAFS has been used to study the local structure of the disordered alloy $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$. These alloys undergo a ferroelectric phase transition from the high-temperature cubic phase of PbTe to the low-temperature trigonal phase of GeTe . The transition temperature is a strong, nonlinear function of Ge concentration,¹ suggesting that the Ge atoms play an important role in the transition. EXAFS studies on the Ge site in these alloys have been performed above and below the transition temperatures for x up to 0.3. The EXAFS results show that Ge atoms are displaced about 0.8 Å from the cell center at all temperatures and Ge concentrations in the both the low- and high-temperature phases.² Because the ions are *always* off-center, this implies that the ferroelectric transition involves long-range ordering of the dipoles, similar to that found in some molecular crystals. Fig. 1 shows a schematic of the order-disorder nature of the transition.³

In addition to the order-disorder character of the transition, there is also a displacive character: EXAFS measurements of the Pb site clearly show that the entire anion sublattice shifts relative to the cation sublattice below the transition temperature. In the EXAFS measurements, this shift is manifested as a splitting of the Pb-Te first-shell distances from six equal bonds to three short and three long bonds. The order parameter of the transition is represented by this splitting, which is shown in Fig. 2. These measurements are the first direct evidence for a simultaneous order-disorder and displacive ferroelectric transition in a semiconductor alloy.

Fig. 1. Two-dimensional schematic of the proposed alignment of off-center Ge ions in (a) high temperature cubic phase, and (b) low temperature trigonal phase. Large circles: Pb, small circles: Ge. The line intersections represent Te ions.

Fig. 2. Mean-square deviation in Pb-Te first-shell distances. The increased distance deviation at low temperatures is due to the cation-anion sublattice shift in $\text{Pb}_{0.72}\text{Ge}_{0.18}\text{Te}$ as a function of temperature.

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Supported by ONR #N00014-85-K-0614. The X11 beamline is supported by DOE #DMR-DE-AS05-80ER10742.

SITE CORRELATIONS IN QUATERNARY III-V SEMICONDUCTOR ALLOYS

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It has become increasingly apparent that the local structure of disordered alloys is more complicated than previously believed, with bond-length distortions or even a tendency for long-range order under some conditions.¹

In this work, we are interested in *local* ordering: specifically, correlated site occupation in disordered III-V quaternary alloys. Although most electronic structure theories of disordered alloys assume complete randomness, there are almost certainly deviations from totally random behavior. For example, in the quaternary alloy $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{Sb}_{1-y}$, the "average" Ga atom will have some mixture of As and Sb nearest neighbors. Because of differences in bonding energies and in atomic sizes, it is unlikely that the number of As atoms as nearest neighbors to the Ga would simply scale as the concentration y .

The samples were prepared by *quenching* from the melt in evacuated quartz ampoules. The materials were then repeatedly ground and annealed at 500C. Compositional uniformity was monitored with x-ray diffraction line widths and electron microprobe analysis.

Our transmission EXAFS measurements for these alloys show large deviations from randomness, with Ga-As pairs being clearly preferred over In-As pairs. For example, for the alloy series $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{Sb}_{1-y}$, with $x = 0, 0.25, 0.50, 0.75$, and 1.0 , and y fixed at 0.1 , we may study the environment about an "average" As atom. The EXAFS results directly reveal the number of Ga atoms neighboring the photoexcited As as a function of composition x . If the alloy were truly random, the number of Ga neighbors would vary linearly with composition. Our results, shown in Fig. 1, show Ga-As pairs are much more common than expected. We have directly determined that Ga-As pairs and In-Sb pairs are preferred over Ga-Sb and In-As pairs, and the "disordered" alloy is actually much more ordered than earlier believed. Samples prepared at lower growth temperatures with CVD or MBE techniques are expected to show even larger correlations. These results are expected to impact calculations of energy levels, electron mobilities, phonon states, and crystal growth.

Fig. 1. The number of Ga neighbors surrounding the "average" As atom in $\text{Ga}_x\text{In}_{1-x}\text{As}_{0.1}\text{Sb}_{0.9}$, as a function of Ga concentration x . The straight dashed line is that expected if the alloy were truly random. This deviation from randomness shows a tendency towards ordering, with Ga-As bonds being preferred over In-As.

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Supported by ONR #N00014-85-K-0614. The X11 beamline is supported by DOE #DMR-DE-AS05-80ER10742.

SHORT RANGE ORDER IN THE ICOSAHEDRAL AND DECAAGONAL PHASES

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We have continued our work reported last year¹ on identifying the structural unit in the icosahedral phase (i-phase) of AlMnSi. The position of the Al atoms in the structural unit is located. We also compared the Fe and Mn sites in the aperiodic Al-(Mn, Fe)-(Si) alloys. We also investigated the stable icosahedral phase - T2 phase of AlCuLi.

We have developed a new method² of analyzing non-gaussian distribution in EXAFS. This method is based on the cumulant expansion and yields the pair distribution function (PDF) by direct Fourier transform. The first shell PDF of Mn in aperiodic Al-Mn-(Si) was obtained using this method.³ Combining these results with the focussing effect in the α (AlMnSi), we are able to locate the Al atoms in the Mackay Icosahedron (MI) which is the structural unit in the i-AlMnSi and i-AlMn.

By a detailed comparison between α (AlMnSi) and i-AlMnSi, we find evidence that the cubic distortion of the MI in the α phase remains in the i-phase.⁴

The connection between the MI was also analyzed³ and we found that the result gives a coordination number of about 7.2 MI as opposed to the 8 in the α phase. This number is significantly higher than those predicted by the random accretion models of the i-phase (which is around four⁵) and the quasicrystalline model of Audier and Guyot⁶ (which is around five).

Based on these results we propose that the i-phase is composed of orientated AlMnSi α -phase microcrystals of size about 40 Å interconnected by the individual, orientated MI units.⁴

We also compared the Fe and Mn sites in the icosahedral Al-(Mn₉₈Fe₂Si) and decagonal Al-(Mn₉₈Fe₂).⁷ While the Fe and Mn sites were found to be the same in the i-phase, we found that they are different in the decagonal phase. These results have implications on the Mossbauer and neutron scattering studies of the aperiodic alloys.

Finally, we investigated the Cu sites in the icosahedral T2-AlCuLi and the bcc R-AlCuLi⁸, we found that the Cu environments in the two phases are almost exactly the same. Based on this and the structure of the R-phase, we proposed a truncated icosahedron of about 100 atoms as the structural unit in the T2 phase, playing a similar function as the MI in the i-AlMnSi. We also proposed that these TI connect through their three-fold axes, similar to the structure of the i-AlMnSi.

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AN EXAFS STUDY OF PYROLYZED METAL MACROCYCLIC ELECTROCATALYSTS

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Absorbed N_4 -chelates of iron and cobalt are known to have electrocatalytic activity for oxygen reduction. However, these materials are unstable and decompose either via hydrolysis in the electrolyte or attack of the macrocycle ring by peroxide intermediates produced during oxygen reduction. Pyrolysis of these materials on carbon at temperatures between 300°C and 1200°C greatly increases the activity and stability of these electrocatalysts.

Electrocatalysts were prepared as follows. The N_4 metal macrocycle was absorbed on high surface area carbon from an organic solvent. The carbon was then dried and pyrolysis was done under an argon atmosphere. Best results have been obtained with cobalt and iron tetramethoxyphenylporphyrin. Previous structural studies on cobalt materials indicate the following. At temperatures of 800°C and above X-ray diffraction results indicate the presence of cobalt metal. At temperatures below 350°C patterns that can be attributed to the original porphyrin material are present. At the intermediate temperatures where the catalytic activity is highest there is no X-ray diffraction pattern.

In the present study pyrolyzed tetramethoxyphenylporphyrins of iron (Fe-TMPP) and cobalt (Co-TMPP) on Vulcan XC-72 (a furnace black carbon) were investigated by EXAFS.

Preliminary results revealed very complicated radial structure functions, indicating the presence of several compounds, including metal and oxides. Chemical leaching of the pyrolysis product removed the metal and oxides and revealed another material which is the electrocatalyst. Figure 1 shows the results for Co-TMPP at 800°C. Also shown are radial structure functions for 7 μ cobalt foil and the unpyrolyzed Co-TMPP on Vulcan XC-72. The results show clearly the complexity of the radial structural function for the as-pyrolyzed material and the similarities between the electrocatalyst and the original starting material. Figure 2 shows that similar results were obtained with the iron material after leaching with HCl or oxalic acid.

Fitting parameters were determined for the first shell of the cobalt material leached with KOH. This yielded values of $N=4.08$, $R=1.93\text{\AA}$ and $\Delta\sigma^2=0.004\text{\AA}^2$. Similar results were obtained for Fe-TMPP pyrolyzed on carbon at temperatures between 600°C and 1000°C.

The EXAFS results indicate that the electrocatalyst consists of the Co- N_4 or Fe- N_4 core of the original macrocycle. The electrocatalytic sites appear to be monodispersed, nitrogen coordinated, Fe and Co atoms.

Fig. 1. Radial structure functions for (a) Co, (b) Co-TMPP pyrolyzed at 800°C, (c) after leaching with KOH, and (d) Co-TMPP.

Fig. 2. Radial structure functions for (a) Fe, (b) Fe-TMPP pyrolyzed at 920°C, (c) after leaching with oxalic acid, (d) after leaching with HCl, and (e) Fe-TMPP.

METAL SUPPORT BONDS IN PLATINUM-CARBON CATALYSTS STUDIED BY EXAFS

W. E. O'Grady (BNL) and D. E. Koningsberger (Eindhoven Univ. of Tech.)

Fuel cell electrocatalysts are based primarily on Pt supported on carbon. The catalytic activity of the electrodes is dependent on both the catalyst particle size and the type of support. In an effort to understand both the role of the catalyst structure and the influence of the carbon support on the catalytic activity, an EXAFS study of platinum supported on carbon has been initiated.

A sample containing 10 wt% platinum was prepared on Vulcan XC-72. At present, Vulcan is the carbon used as the catalyst support in phosphoric acid fuel cells. The EXAFS data were recorded at beamline X-11A on three samples: On the sample as prepared; after reduction in hydrogen at 20°C for 1 hour and after reduction in hydrogen at 250°C for 1 hour.

Analysis of the data from the as-prepared sample gave a Pt-Pt bond distance of 2.77Å as well as an oxidic Pt-O bond distance of 2.07Å indicating a partial oxidation of the platinum particles. Also, a long bond of ~2.67Å was found. This long bond is attributed to the interaction of the platinum with the carbon support.

The analysis of the data from the sample reduced in hydrogen at 250°C for 1 hour gave a Pt-Pt bond distance of 2.75Å and no Pt-O bonds were observed. In this sample two long bonds were observed one at 2.58Å and one at 3.40Å. The bond length of 2.58Å is 0.1Å shorter than that observed in either of the other samples suggesting a tighter binding of the platinum particle to the carbon surface. Since only platinum and carbon are present in the gas treatment cell the bond distance of 3.40Å must be indicative of the formation of an additional platinum carbon bond. This would suggest some change has occurred in the relationship between the platinum particles and the carbon.

The as-prepared sample shows a Pt-Pt coordination number of 5. When this (relative) coordination number of 5 is corrected for the fact there are two types of platinum in the sample, a real coordination number between 5.5 and 6.5 is obtained. The sample reduced at 250°C shows a coordination of 10.5. The treatment given to this sample was quite severe and led to a significant growth in the particle size as evidenced from the increased coordination number. The coordination number for the 20°C reduced sample was 6.5. The increase in coordination number found here is due to the reduction of the surface oxide.

These reduced samples, while not characteristic of in situ fuel cell catalysts have allowed us, for the first time, to observe the interface between a metal and a carbon support.

Support for the development of beamline X-11A and partial support for this research was provided by the Department of Energy under contracts DE-AS05-80ER10742 and DE-AC02-76CH00016.

EXAFS INVESTIGATIONS OF NICKEL HYDROXIDES

K. Pandya, R. Hoffman (Case West. Res. U.), W. O'Grady, J. McBreen (BNL) and D. Corrigan, (GM)

Transition metal oxides and hydroxides are of great technological importance in many electrochemical areas such as batteries, fuel cells, electrolyzers, photoelectrochemical devices and electrochromic devices. Even though transition metal oxides and hydroxides have been studied extensively the structure of many of these materials is poorly characterized. One such example is nickel hydroxide, which employed in the nickel-zinc, nickel-cadmium and nickel-iron batteries. The structure of the nickel hydroxides depends upon the method of preparation. There are two main classes of structure, the well crystallized β -Ni(OH)₂ phase and a poorly crystallized hydrated α -Ni(OH)₂ phase. The β -Ni(OH)₂ crystallizes in the C6-brucite type structure, which is a layered structure with each layer made up of a hexagonal arrangement of nickel atoms octahedrally coordinated by oxygen atoms. The layers are stacked along the c-axis and the O-H bonds are parallel to the c-axis. β -Ni(OH)₂ is well characterized by X-ray and neutron diffraction. The α -Ni(OH)₂ on the other hand gives very diffuse and ill defined diffraction patterns. The structure proposed for α -Ni(OH)₂ is of the brucite type with water and foreign metal ions included in the structure. Hence, the stoichiometry of this hydrated nickel-hydroxide depends on the experimental conditions and can be highly variable and is often denoted as Ni(OH)₂ · xH₂O. The structures of α -Ni(OH)₂ and β -Ni(OH)₂ were investigated using EXAFS.

The β -Ni(OH)₂ was obtained as a reagent grade crystals from Alfa Products and the α -Ni(OH)₂ was prepared by electroprecipitation from a 0.1M Ni(OH)₂ solution. These materials were mixed with boron nitride and pressed to make self-supporting wafers for use in the EXAFS measurements. The EXAFS data were recorded on beam line X-11A at the NSLS.

The radial structure function (RSF) for both the α and β -Ni(OH)₂ consisted of three peaks arising the first peak from the coplanar first Ni-O shell, the second peak from the first Ni-Ni shell and the third peak from the third Ni-Ni shell, as shown in Figure 1. The data are summarized in Table I. The Ni-Ni peaks in α -Ni(OH)₂ are shifted to lower R values indicating a slight contraction of the lattice. However, there is no shift in the Ni-O distances. In the case of β -Ni(OH)₂ the interatomic distances Ni-O and Ni-Ni derived from X-ray data are 2.14Å and 3.13Å respectively. The EXAFS data are in excellent agreement with the Ni-Ni distance giving a value of 3.13 ± 0.01 Å. However, the Ni-O distance found from the EXAFS data is 2.07 ± 0.01 Å shorter by about 0.08Å. Also, a set of molecular force calculations have suggested a lower value for the Ni-O distance of 2.09Å. So there seems to be some question about the 2.14Å XRD value.

The third shell in the RSF of β -Ni(OH)₂ is unusually strong and coincides with the third coplanar Ni-Ni shell at 6.26Å. This peak, which is unusual, probably arises from the multiple scattering focussing effect.

Support for the development of beamline X-11A and partial support for this research was provided by the Department of Energy under contracts DE-AS05-80FR10742 and DE-AC02-76CH00016. Partial support for this work by NASA under Grant No. NAG-3-694 is also gratefully acknowledged.

Structural Parameters Obtained from the EXAFS Analysis
Using NiO as the Reference Compound

Sample	Temp. °K	Shell	N	R, Å	$\Delta\sigma^2$, Å ²
β -Ni(OH) ₂	77	Ni-Ni	6.23	3.30	.0002
		Ni-O	5.96	2.07	-.0012
		Ni-Ni	6.77	6.26	.0018
	297	Ni-Ni	6.00	3.12	.0026
		Ni-O	5.86	2.07	.00037
		Ni-Ni	6.02	6.26	.00539
α -Ni(OH) ₂	77	Ni-Ni	5.68	3.08	.0024
		Ni-O	5.55	2.05	.0009
	297	Ni-Ni	5.30	3.08	.0049
		Ni-O	6.24	2.05	.002

Estimated Errors: $\Delta N = \pm 10\%$, $\Delta\sigma^2 = \pm 15\%$, $\Delta R = \pm .01$ Å

Radial structure functions for α -Ni(OH)₂ and β -Ni(OH)₂. For α -Ni(OH)₂, Ni-Ni peaks are shifted towards lower R- values indicating a contraction in bond distances.

BONDING AND COORDINATION IN STUDIES OF CRYSTALLINE AND AMORPHOUS TRANSITION METAL ALLOY SYSTEMS

D. M. Pease, D. Brews, Z. Tan, M. Choi and J. I. Budnick (U. of CT)

The β phase transition metal aluminides are high temperature, light alloys which are, unfortunately, also brittle. In order to elucidate the bonding characteristics of these materials, transition metal K edge EXAFS were obtained over a broad temperature range for β phase, stoichiometric NiAl, CoAl, and FeAl. We find that the Ni-Al and Co-Al bonds have comparable vibrational amplitudes, but the TM-TM bonds in Co-Al are stiffer than corresponding bonds in Ni-Al. Our analyses of Fe-Al is not yet complete, but the EXAFS results are intriguing in light of the metallurgical experience that CoAl is decidedly the most brittle alloy of this series.

Our EXAFS studies of the amorphous $(\text{Ni}_{100-x}\text{Pt}_x)_{75}\text{P}_{25}$ system allowed us to identify three subshells in the Pt EXAFS corresponding to the Pt-Pt, Pt-Ni and Pt-P coordinates. We find from a systematic study of the temperature dependence that the structural disorder is less for Pt-Pt than for Pt-Ni pairs, though the thermal disorder is greater for Pt-Pt pairs. The Pt-Pt distance is close to that found for metallic Pt. In this structure the Ni atoms are found to have a larger basic disorder in their positions than the larger and more tightly packed Pt atoms. This work will appear in Phys. Rev. B. Oct. 1987.

Acknowledgement

This work was performed at Beam Line X-11 at the NSLS and is supported by the Division of Materials Science of DOE under Contract No. DE-AS05-80-ER10742.

BOND LENGTHS IN $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$

W.-F. Pong and B. A. Bunker (Notre Dame), U. Debska (Purdue), and J. K. Furdyna (Purdue and Notre Dame)

In this project, EXAFS has been used to determine bond lengths in the diluted magnetic semiconductor $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$. The magnetic Mn ions in the alloys couple to one another through a super-exchange mechanism involving the Se ions, and also couple directly to the band electrons giving rise to unique electrical, magnetic, and optical properties.¹ The alloys change from a cubic (zincblende) crystal structure to a hexagonal (wurtzite) structure as a function of composition, with the transition at $x \sim 0.3$.² Although x-ray diffraction measurements show the lattice parameter to change by approximately 0.2 Å through the series, the nearest-neighbor bond distances show no change within the experimental uncertainty of 0.01 Å.

The samples used for this work were all grown using the Bridgeman growth technique using an rf-induction-heated graphite crucible.³ For these measurements, the samples were ground to a fine powder sieved through 400 mesh. The EXAFS spectra were obtained in transmission mode at the National Synchrotron Light Source using the X11A beam line. Both the Zn and Mn edges were measured at room temperature for samples of concentration $x = 0.15, 0.35, 0.57$. As standards in the analysis, the Zn edge of pure ZnSe and the Mn edge of cubic MnSe were also measured.

The EXAFS results are summarized in Fig. 1. These results show that the local crystal structure is highly distorted from the average "virtual crystal", and this distortion is insensitive to the differences between the cubic and hexagonal phases. The resultant distortion of the tetrahedral bond angles is also expected to strongly affect the super-exchange coupling between magnetic ions.

Fig. 1. EXAFS results for Zn-Se bond distance (lower circles); EXAFS results for Mn-Se bond distance (upper circles); x-ray diffraction determination of cation-cation distance, multiplied by $(3/8)^{1/2}$ (circles); and linear fit to diffraction results (dashed line).

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Supported by ONR #N00014-85-K-0614. The X11 beamline is supported by DOE #DMR-DE-AS05-80ER10742.

METAL IMPURITIES IN COAL AND ITS COMBUSTION PRODUCTS

C. L. Spiro (General Electric) and Joe Wong (Lawrence Livermore National Laboratory*)

As part of a major U.S. Department of Energy initiative to develop coal as an engine fuel, General Electric has contracted to examine both diesel and gas turbine engines fired on coal. A primary impediment to commercialization of coal-fired engines is the indigenous coal minerals which may become corrosive, erosive, abrasive, adherent, or polluting as a result of combustion.

We have employed x-ray absorption spectroscopy to characterize the form and fate of coal-borne impurities from the mine, through beneficiation, and in samples taken at various engine locations and conditions. We have focussed on potassium¹ which is corrosive in some forms, iron which forms deposits and respirable vapors, and calcium which influences both deposition and gaseous sulfur emissions. Our major accomplishments have been to show that potassium occurs in an aluminosilicate clay, and fuses to a relatively benign, non-corrosive feldspathoid-like glass. Calcium was found to rapidly sorb sulfur in the engine, suggesting a means to prevent acid-rain precursor formation. On the other hand, calcium was found to partition between sulfate and aluminosilicate moieties, and strict composition and thermal parameters must be adhered to in order to prevent catastrophic deposition. Iron participates through both stable hematite and a reactive aluminum spinel. The aluminum from the latter combines with calcium to form a tenacious anorthitic deposit when threshold temperatures are exceeded.

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*Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

LOCAL MELTING ABOUT IMPURITIES

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X-ray absorption fine structure (XAFS) measurements¹ were made on pure Pb and a 5 at % solution of Hg in Pb. Changes in the mean square displacement $\Delta\sigma^2$ between both Hg and Pb atoms and their nearest neighbors were measured between low temperatures and bulk melting temperature. The results are shown in the Figure. The solid points are the temperature dependence of the measured values of $\Delta\sigma^2$ for the Pb atoms relative to 10K. The solid curve is the variation expected for an Einstein oscillator of Einstein temperature 71K. The open points are the measured values of $\Delta\sigma^2$ as a function of temperature for the Hg impurity atoms relative to 30K. The lower portion of the dashed curve is the variation expected for an Einstein oscillator of characteristic temperature 60K. Above 400K the dashed curve is only to show the trend of the points. The top points with the symbol of an "x" are the apparent coordination numbers about the Hg impurities versus temperature. The dashed curve through these points is only to show the trend of the points. The bulk melting temperatures for the two samples are indicated by the arrows.

Whereas the variation of $\Delta\sigma^2$ for the Pb atoms is as expected for an atom in a solid, namely, a monotonic increase of $\Delta\sigma^2$ versus T , the variation for Hg atoms shows a non-crystalline behavior above 400K.

To interpret this non-crystalline behavior we note the following: Adding zero point motion to $\Delta\sigma^2$ we find σ_m^2/d^2 , the mean square disorder at melting divided by the square of the nearest neighbor distance, equals 0.0045(2) for Pb atoms, similar to the value around the Hg impurities of 0.0045(2) at 400K. Thus the Hg impurities lose their non-crystalline behavior at the Lindemann critical value where Pb melts. The decrease in the apparent coordination and the leveling off of the $\Delta\sigma^2$ around the Hg impurities is similar to the local behavior around Pb atoms as pure lead melts. The decrease in apparent coordination number at melting occurs because diffusion increases by a factor of 10^4 so that about 1/3 of the time Pb atoms are diffusing and their XAFS during that time is invisible because of the large spread in nearest neighbor distances.

Since locally the Hg impurities above 400K show similar behavior to Pb atoms as bulk melting occurs, yet bulk melting hasn't occurred in the alloy, we interpret the results as a local melting about the Hg impurities starting at 400K, about 180°C below bulk melting.

The mechanism found for the Pb:Hg solid solution may also be applicable to pure materials. Defects always occur in pure materials: thermally generated point defects such as vacancies; inherent ones in the sample such as dislocations, grain boundaries and surfaces. One expects, in general, that the atoms in the vicinity of such defects will have larger amplitudes of vibrations. Then the same mechanism of local melting is expected around these defects. Phenomena which can be interpreted as local melting have already been experimentally detected around surfaces^{2,3} and grain boundaries⁴. It is of interest to note that Nachtrieb suggested a melted region around diffusing atoms in crystalline metals⁵.

The question remains, which defects dominate the nucleation of the bulk melting of pure materials. As the linear dimensions L of the sample increases, the surface melting volume should grow as L^2 while the local melting volume around point defects should grow as L^3 . Thus, in the thermodynamic limit, the melting process should be dominated by nucleation about point defects.

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g u e

The lower points associated with the left axis are plots of the change with temperature of mean square disorder $\Delta\sigma^2$ relative to 10K for Pb atoms in pure lead (solid points) and relative to 30K for Hg impurities in a lead host (open points). The curves are the calculations of Einstein oscillators of Einstein temperature 71K (solid) and 60K (dashed till 400K). The top points associated with the right axis are the apparent coordination numbers about the Hg impurities versus temperature. The dashed curve is only to show the trend of the points. The bulk melting temperature for the two samples are indicated by the arrows.

GLANCING ANGLE EXAFS STUDY OF Al/Nb INTERFACE REACTIONS INDUCED BY ION BEAM IRRADIATION.

Z. Tan, J. I. Budnick, D. Pease (U. of CT), S. M. Heald, J. Tranquada (BNL)

We have applied both fluorescence and reflection EXAFS to study the interfacial reaction between niobium and aluminum thin films prepared by sequentially sputtering niobium and aluminum onto float glass in ultra-high vacuum. The X-rays were adjusted to be incident at angles greater than the critical angle of Al but less than that of Nb, such that the interface region of the Al overlayer and niobium is probed. In a narrow range of incident angles, both reflection and fluorescence signals yield EXAFS spectra of equal quality. Due to anomalous dispersion of the optical constants, the coordination number cannot be reliably obtained without properly correcting the distortion in the amplitudes. Our results indicate that this correction has to be carried out separately for reflection and fluorescence. The near neighbor distance (R) determined from reflection EXAFS and fluorescence EXAFS are the same within the expected error of the R determination in standard EXAFS, but the value of σ^2 extracted from the fluorescence EXAFS tends to be smaller in most cases.

A comparison of the EXAFS functions and their Fourier transforms of the as sputtered Al/Nb/float glass sample to those of bulk niobium (measured by transmission) revealed no other phases except bcc niobium in the interface region of Al and Nb. Therefore any compound formation during the sputtering and later thermal diffusion could not be detected and is expected to be small. Part of the Al/Nb/float glass sample was irradiated at room temperature with Al^+ ions of energy 50 keV at a low dose rate to a total dose of $1 \times 10^{16} \text{ Al}^+/\text{cm}^2$. A Rutherford backscattering measurement can barely see any composition change in the interface region. The EXAFS oscillation from the interface region dies out above $k = 10 \text{ \AA}^{-1}$. The Fourier transforms show very little contribution from near neighbors beyond $3.5 \text{ \AA}$. We believe that large disorder may be present in the ion beam mixed region, perhaps the phase formed is amorphous. We could tentatively assign the Al and Nb backscatter contribution to the Fourier transform magnitude in R space. From our data we estimated the near neighbor distances without taking into account any possible large disorder, using the Nb-Nb and Nb-Al phase shifts determined from model compounds. At extremely small penetration, the Nb nearest neighbors are dominantly Al atoms at an average distance of $3.1 \text{ \AA}$. As the penetration increases, Nb atoms start to show up at $\sim 3.0 \text{ \AA}$ from the Nb absorber. This Nb-Nb distance is close to that in Nb_2Al ($R_{\text{Nb-Nb}} = 3.04 \text{ \AA}$), but the Nb-Al distance both for low and high penetration is greater than that in the Nb-Al compounds (NbAl_3 , Nb_2Al and Nb_3Al . All have an Nb-Al bond length of $\sim 2.89 \text{ \AA}$).

On a Al/Nb/float glass sample irradiated to a dose of $1.5 \times 10^{17} \text{ Al}^+/\text{cm}^2$, the Nb K-edge EXAFS oscillations from the interface persist into high k region. However their Fourier transforms are damped out beyond $3.5 \text{ \AA}$, which suggests the lack of long range order in the ion mixed interface region. Analysis of the low R part of Fourier transform is in progress. It is somewhat different from that found in the low dose case.

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Acknowledgement

This work was performed at Beam Line X-11 at the NSLS and is supported by the Division of Materials Science of DOE under Contract No. DE-AS05-80-ER10742.

THE OXIDATION OF Fe(II) DURING FERRITIN FORMATION: AN X-RAY ABSORPTION STUDY LEADING TO A REEVALUATION OF THE FUNCTION AND THE EVOLUTIONARY AGE OF THE PROTEIN

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Ferritin is a protein found in plants, animals, and bacteria that stores iron in a soluble, non-toxic form. It consists of a protein coat surrounding a core of polynuclear hydrous ferric oxide of as many as 4500 Fe(III) atoms. At one time, ferritin was thought to be the response of organisms to the accumulation of dioxygen in the atmosphere starting ca. 2.5 billion years ago. However, experiments during the last year, using dispersive x-ray absorption spectroscopy at LURE and conventional x-ray absorption spectroscopy at NSLS (Beam Line X-11), have caused a reevaluation of the role of ferritin. The results, described in a preliminary fashion [1], suggest that ferritin may be a very old protein associated with the most primitive living organisms.

Our experiments, based on earlier concepts that the protein coat of ferritin catalyzed the conversion of Fe(II) to polynuclear Fe(III), were designed to measure the rate of oxidation of Fe(II) in the presence of the protein using difference in the XANES between Fe(II) and Fe(III) as an assay. Because of the speed of the reaction predicted from indirect analyses of the Fe environment, we performed our experiments on the dispersive line at LURE. However, we discovered that the previous ideas were incorrect, and that the formation of the ferritin iron core was very slow. The reaction was only 40% completed after 13 hours. We were able to finish the experiments using conventional x-ray absorption on the X-11 Beam Line at NSLS. Up to 24 hours were required for oxidation and core formation to be complete, in contrast to the 1-2 hours previously deduced. The reaction conditions were comparable to those in living tissues in terms of the Fe/O₂ ratio, and suggest that, *in vivo*, the protein coat of ferritin may actually STABILIZE Fe(II).

X-ray absorption spectroscopy of ferritin iron core formation, which allowed us to examine the Fe environment in ferritin under conditions comparable to those *in vivo*, led to the following new ideas about ferritin function:

1. The role of ferritin in primitive organisms, even in the absence of dioxygen, may have been the sequestration of iron to prevent promiscuous electron transfer to biologically important organic molecules and the formation of free radicals in, e.g., lipid membranes and nucleic acids.
2. The electron flux required for Fe metabolism through ferritin in cells which rapidly recycle iron *in vivo* may be greatly minimized if some of the iron remains as Fe(II) while in ferritin; the energy demand associated with Fe metabolism would thus be greatly reduced.
3. The formation of magnetite particles in organisms such as magnetic bacteria and birds may proceed from the partial oxidation of Fe(II) in ferritin rather than the partial reduction of Fe(III) as previously believed.
4. Ferritin can provide a model for studying the control of corrosion as hydrated Fe(II) and Fe(II)(OH)₂ are converted to Fe(III)OH and Fe₂O₃.

Next year the conditions which influence the oxidation of Fe(II) in ferritin, such as pH, buffer anions, and electron acceptors, will be examined using XANES of the Fe edge. In addition, the influence of the ferritin protein coat will be investigated using proteins from cloned DNA engineered for expression in *E. coli*. Preliminary experiments show that such proteins can form ferritin iron cores, but with slightly altered properties.

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Supported in part by NIH Grants DK20251 and GM34675.

RARE EARTH IONS IN FLUORIDE LASER GLASSES

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EXAFS was used to test computer simulations of the local structure of rare-earth-doped Be fluoride glasses of interest for laser applications. Simulations were performed using molecular dynamics and simple interionic pair potentials. Although the quenching rates in the simulations are extremely fast because of computer limitations, previous EXAFS studies of the Nd^{3+} in simple BeF_2 showed that the general features of the local structure were correct. The simulations also predicted that for more complex glass compositions, the fluorine coordination number about the rare earth should increase. This was confirmed from x-ray fluorescence measurements of the EXAFS oscillations of the L_3 edge for Nd-doped $\text{BeF}_2 \cdot 55\text{BeF}_2 \cdot \text{RF}$ ($\text{R} = \text{Li}, \text{K}, \text{Rb}$) and a multicomponent glass $34\text{BeF}_2 \cdot 19\text{MgF}_2 \cdot 10\text{CaF}_2 \cdot 14\text{BaF}_2$ glasses. This feature can be used in tailoring the spectroscopic properties of laser glass.

Table I. White line analysis of the normalized Nd L_3 XANES.

BASE GLASS (mol.%)	PEAK HEIGHT	LINEWIDTH (eV)	INTEGRATED INTENSITY
100BeF_2	2.83	5.71	24.3
$55\text{BeF}_2 \cdot 45\text{LiF}$	3.14	5.35	25.7
$55\text{BeF}_2 \cdot 45\text{KF}$	3.81	4.57	27.3
$55\text{BeF}_2 \cdot 45\text{RbF}$	4.04	4.59	28.5
$34\text{BeF}_2 \cdot 23\text{AlF}_3 \cdot 19\text{MgF}_2 \cdot 10\text{CaF}_2 \cdot 14\text{BaF}_2$	4.05	4.62	29.1

Fig. 1. Whiteline Analysis of Nd L_3 XANES into a Lorentzian and an arctangent component.

*Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

METALS IN β -BORON

Joe Wong (Lawrence Livermore National Laboratory*) and Glen A. Slack (General Electric)

Beta-boron is a semiconductor with a band gap of ~ 1.5 eV. It is hard and refractory with a very high melting point of 2300 K. It satisfies the "small atom and large number of atoms per unit cell" criterion for potentially high thermoelectric efficiency. Crystallographically, beta-boron is made up of compact B_{12} and B_{10} polyhedral units and isolated B atoms, all linked together by strong, directional covalent bonds. These structural and bonding features create a very open structure in beta-boron. With a boron radius estimated to be 0.88 Å, the degree of space filling is calculated to be only 36%. Consequently, the structure contains many holes that can interstitially accommodate a variety of metal atoms in the Periodic Table. The doped boron materials may be denoted by $B_{100-x}M_x$, where M may be a transition or non-transition metal and x can vary from fraction of, to a few atomic % depending on solubility at the doping conditions at high temperature and pressure. We have undertaken a systematic XANES study of the 3d metal sites and their concentration variation in beta-boron. The effect of double doping in two V/Cu-doped materials have also been examined. Chemical and structural information of this kind are much needed to gain insight into the understanding of physico-chemical behavior that are relevant to improved and advanced radioisotope nuclear power thermoelectric applications.

In Fig. 1, the normalized XANES spectra are shown for a series of 3d metals, 1 atomic % in concentration, doped in beta-boron. The energy zero is taken with respect to the first inflection point of the corresponding pure metal in the respective derivative spectrum. For the early transition metals, Ti, V and Cr in particular a number of well-resolved features up to 24 eV are evident. The pre-edge features at 1-2 eV is a $1 \rightarrow 3d$ transition, which normally is dipole forbidden, but is rather strong, indicative of appreciable p overlap with the d states of the metal dopant. Two well defined bound states at 7 and 11 eV are also evident. The principal maximum at ~ 23 eV is due to lattice scattering from the boron neighbors. As the d-states are progressively filled in going across the 3d series from Ti to Cu, the pre-edge feature at 1-2 eV becomes less well-defined as is seen from the XANES of Mn and Fe. The pre-edge feature almost disappear in the spectra of Co, Ni and Cu. At the same time the doublet feature below 10 eV becomes less resolved and merges to a shoulder on the steeply rising edge. This is again evident from the spectra of Mn through Cu. The principal absorption maximum decreases in energy from Ti to Cu, implying an increase in the metal-boron separation.

The concentration dependence of the XANES spectra is also of interest, and may be correlated with the progressive occupancy of various interstitial sites, i.e., the A site first, then E and D sites in that order with increasing concentration. This behavior is exhibited in V, Ni and Cu. In the case of Cu changes in the XANES spectrum occur at above 1% doping. This is even more pronounced than that for Ni in that the 26.6 eV feature disappears altogether at 3% doping, being replaced now by an absorption minimum. This correlates well with occupancy of a second Cu site as determined by x-ray crystallography.

*Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

Fig. 1. Normalized K-edge XANES Spectra of 1 at % 3d metals doped in β -Boron.

X-RAY ABSORPTION STUDIES OF VANADIUM IN FCC CATALYSTS

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X-ray Absorption Spectroscopy was used to investigate the oxidation state and local environment of vanadium in Fluid Catalytic Cracking (FCC) catalysts subjected to conditions simulating reaction and regeneration in an FCC unit. Vanadium and nickel, which deposit on catalyst during reaction, are detrimental to catalyst performance due to promotion of dehydrogenation reactions which increase coke make and light gas yield at the expense of gasoline production. Additionally, vanadium is known to cause zeolite structural degradation leading to irreversible loss of catalyst activity. Commercial FCC catalysts containing USY and REY were used in this study and vanadium near edge structure was monitored and compared with catalyst activity.

Microunit studies show that vanadium remains in the +4 oxidation state after cracking but converts to V^{+5} during catalyst regeneration. Identical V-edge data were observed using gas oil feeds doped with V naphthenate, vanadyl porphyrin, or a high metals containing crude oil (Boscan), indicating insensitivity to vanadium source. V-doped catalysts deactivated over a wide range of conditions leads to chemically similar V^{+5} species although cracking activity decreases with increasing severity. These results suggest that oxidation of vanadium is not solely responsible for catalyst deactivation but that other factors, such as V location and mobility, play an important role in deactivation phenomenon. Basic alkaline earth oxide passivators such as MgO, admixed to the catalyst, strongly interact with the vanadium during the regeneration period. Although the oxidation state of V is essentially unaffected, MgO structurally modifies V as evidenced by a unique absorption spectrum. This species has been identified as a magnesium vanadate compound.

*This work was performed on beamline X-11A at the NSLS and is supported by the Division of Materials Science of DOE under Contract No. DE-AS05-80-ER10742.

C. Y. Yang, J. M. Lee, M. A. Paesler, and D. E. Sayers (NC State U.)

We report¹ the first direct and quantitative structural information associated with the photo-structural change in α -As₂S₃. EXAFS experiments were performed on samples that had undergone three reversible and reproducible cycles of thermal annealing and light soaking. A reversible red-shift of the optical edge (i.e. photo-darkening) in light-soaked films was confirmed by optical transmission measurements as shown in Fig. 1. Measured changes induced by light include: i) an increase in the atomic percentage of wrong (As-As) bonds from 1.5% to 2.0%, ii) an enlargement of θ , the mean As-S-As bond angle, from 99.5° to 100.3°, iii) a 2° increase in the spread of the angle θ ; and iv) an absence of any changes in the 3rd shell As-S distance. The 33% change in the number of wrong bonds alone would result in a fractional increase in volume $\Delta V/V = 0.3 \times 10^{-3}$. In Fig. 2, the first peak of the radial structural function for α -films arises from As scattering at 3.48 Å for annealed films and 3.5 Å for light soaked films. The observed 2.0×10^{-2} Å increase in the As-As distance can be shown to result in a fractional increase of $\Delta V/V = 5.7 \times 10^{-3}$. The total increase in volume fraction from the EXAFS data is therefore 6.0×10^{-3} , which is exactly what has been measured. Although this precise agreement must certainly be considered somewhat fortuitous, we feel that these data provide the first quantitative correlation between microscopic structural measurements and macroscopic measurements of the photo-induced effect. Because of an interplay between the photo-structural changes and the photo-expansion measurements, it is suggested² that the dominant mechanism of the photo-induced changes involves a twisting of adjacent AsS₃ pyramids about their shared S atoms as well as an expansion of the As-S-As angle at that shared atom.

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Fig. 1. Optical absorption edges of virgin (solid line), annealed (dashed line) and light-soaked (dotted line) α -As₂S₃ films. The cycles are indicated by arrows. Photo-darkening and annealing cycles were reproducible and reversible for cycles 2 through 7.

Fig. 2. Expanded view of the As-S phase corrected Fourier transform for the second (opened circle) and third cycle (dashed line) of the annealed films and the second (starred line) and the third cycle (solid line) the light-soaked films. This is to demonstrate the reproducibility and reversibility of photo-structural changes in the second and third shell contributions.

NOTE: This research was supported by the U.S. DOE under Contract No. DE-AS05-80-ER10742 and NSF Grant DMR-8407265.

THE USE OF AN ULTRA-HIGH RESOLUTION MONOCHROMATOR FOR NUCLEAR BRAGG SCATTERING

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A new apparatus for the study of nuclear Bragg scattering has been developed at beam line X12A. The system comprises an ultra-high resolution monochromator feeding a 2-circle diffractometer. The 14.41 keV Mossbauer resonance of ^{57}Fe in an isotopically enriched and highly perfect Fe_2O_3 crystal was successfully excited using the beam from this monochromator as a probe.

Fig. 1. Schematic arrangement of the high-resolution monochromator and nuclear resonant sample.

Figure 1 shows the general arrangement of the apparatus. The first optical element is a silicon (111) monolithic double reflector [1] whose main function is to isolate the later high resolution elements from the thermal load of the synchrotron white beam. The second and third elements are also silicon monoliths, but cut to provide very high order diffraction planes in order to maximize the resolution. The planes used were the (10,6,4) planes, giving a resolution of 0.005eV at 14413eV, with an angular divergence of the output beam of around 0.5 arc-seconds.

The requirement for such high resolution stems from the extreme narrowness of the Mossbauer line (of order 10^{-7} eV). In order to detect resonant photons, the background of non-resonant photons must be as low as possible. If a conventional monochromator is used, (providing a bandwidth of a few eV), the ratio of non-resonant to resonant photons incident on the nuclear scattering sample is around 10^8 . Much of this can be rejected by judicious choice of the scattering sample. Our experiment used antiferromagnetic Fe_2O_3 , [2] which has the property that certain Bragg reflections have zero electronic scattering factor, but non-zero nuclear scattering. Such reflections are termed 'pure-nuclear'. Incoherent processes still prevent one from reaching such good signal-to-noise ratios, and this is where a reduction in non-resonant input flux can be beneficial. It decreases the noise level (by a factor of 1000 or so) but only slightly reduces the signal level.

Fig. 2. Angle rocking curves of a normal Bragg peak, the (6,6,6), and nuclear resonant Bragg peak, the (7,7,7). The angular widths are almost identical.

Fig. 3. Energy scans through the (6,6,6) and (7,7,7) peaks. Note the striking difference in widths, demonstrating the nuclear nature of the latter.

Using this apparatus, we were able to isolate a very pure beam of resonant photons of intensity >2 photons per second and signal-to-noise ratio 100:1, using the pure-nuclear (7,7,7) reflection of Fe_2O_3 (rhombohedral indices). Figure 2 shows angle rocking curves of the Bragg peaks found at the resonance energy for the pure-nuclear (7,7,7) and the normal (electronically allowed) (6,6,6) reflection. They are very similar in width, indicating that the width is dominated by crystal perfection. Figure 3 shows an energy scan through the pure nuclear reflection, contrasted with a similar energy scan for the electronically allowed reflection, the (6,6,6). The energy width of the latter is dominated by the sample crystal reflection width, as dictated by Bragg's law. The energy width of the (7,7,7) is dramatically different, and is in fact dominated by the monochromator resolution function. If this feature was of an electronic nature, it would show an energy width similar to that of the (6,6,6), and so this data indicates that we are indeed observing nuclear Bragg scattering. A similar feature was also observed at the (5,5,5) position, having identical energy and bandwidth.

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BEAMLINE X-12C

A BROOKHAVEN BIOLOGY FACILITY FOR MEASUREMENT OF SINGLE CRYSTAL DIFFRACTION DATA FROM PROTEIN CRYSTALS,

Robert M. Sweet and Donna M. Cyr (Biology Department, BNL)

Beamline X-12C has been developed by the Biology Department at BNL for measurement of diffraction data from crystals of biological macromolecules. It features a horizontally focused beam in the energy range 8 - 12 kv. The data-collection technique used is rotation photography, and this is very conveniently accomplished with the instrumentation and darkroom that have been provided.

The great majority of users of beamline X-12C are visitors from other research institutions. The work done here represents a tiny fraction of the total effort required to obtain the three-dimensional structure of a biological macromolecule. For example, a trip to Brookhaven is rarely undertaken until substantial effort has been invested in specimen preparation, a process which could take a few years work. The data measured in 8 shifts of beam-line use could comprise over 300 individual x-ray films. It could easily take 2-3 man-months of work for digitization and primary data reduction to be performed on these films, and another 6-12 months could be required to interpret fully the results that follow from the data.

Although the x-ray beam was available for only 17 weeks during fiscal 1987, the facility was in use for 125 shifts during this time. Heavy users were groups from NASA, Oxford Univ., Univ. of Calif. San Francisco, MIT, UCLA, and Johns Hopkins. This represents a tremendous quantity of data collection. Many of these visitors were able to measure diffraction data for complete protein crystal structures in two days' work or less. Several, including members of the PRT, measured quite high-resolution data, say to 1.9 Å resolution.

Significant scientific results.

1. The structure of a bacterial photosynthetic reaction center has been determined: data were measured at NSLS to 2.8 Å resolution and the structure has been refined to a crystallographic residual of $R = 26\%$ (Rees and co-authors).¹
2. The structure of the protein inhibitor from potatoes of the enzyme carboxyptidase has been refined to high resolution. Data were measured to 1.9 Å resolution and the refinement residual is $R = 19\%$. Rees, UCLA.
3. The binding sites for phosphate ion alone and phosphate and glucose together have been found in phosphorylase a. Hajdu, Oxford. This research was supported by the Office of Health and Environmental Research and by the U.S. Department Of Energy.

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PHASON STRAIN IN ORIENTED QUASICRYSTALS

J. D. Budai, J. Z. Tischler, A. Habenschuss, and G. E. Ice, (ORNL); and V. Elser (AT&T Bell Labs)

A large number of studies have investigated the structure of icosahedral quasicrystals which were first discovered in rapidly cooled alloys¹. Despite these studies, the atomic arrangements comprising a quasicrystal are not well understood. In our studies of alternative techniques for producing quasicrystals, we have found that the icosahedral grains formed by implanting Mn ions directly into Al single crystals display a unique orientation with respect to the fcc matrix². Since the quasicrystal grains are aligned, these ion-implanted samples are suitable for "single quasicrystal" x-ray diffraction studies.

High-resolution x-ray diffraction measurements obtained from these samples surprisingly show that the quasicrystal Bragg peaks do not lie at positions of exact icosahedral symmetry. Recent theoretical treatments³ have shown that systematic peak shifts can be associated with the presence of a linear phason strain, a form of disorder not possible in ordinary crystals. An analysis of our data shows that, in one case, the observed positions of 37 different peaks can be quantitatively described by a diagonalized linear phason strain matrix containing only two independent parameters⁴. Figure 1 shows examples of the oscillatory peak shifts along particular symmetry axes which result from a linear phason strain. Also plotted are the peak shifts predicted by Pauling's alternative icosatwin model⁵. Clearly, the predictions of his model are inconsistent with our measurements. We find that the peak shifts observed in all ion-implanted samples cannot be described by the same phason strain matrix. This observation is to be expected since the phason disorder should be correlated with the growth conditions for different quasicrystal grains.

In addition to providing the shifts, our x-ray diffraction measurements show that the quasicrystal Bragg peaks are fairly broad ($\geq 0.015 \text{ \AA}^{-1}$). However, the variation in width for different peaks does not simply increase with larger reciprocal lattice vector, $|G|$ as is expected for random strains in an ordinary crystal. Instead, the peaks also show larger widths with increasing phason momentum, $|G_{\perp}|$. This result is similar to the observations of Heiney et al.⁶ in AlCuLi quasicrystals and indicates the presence of either nonlinear components in the phason strain or the superposition of scattering from different grains with slightly different linear phason strain.

Fig. 1. Shift in peak position $|G|$ along twofold icosahedral axes (A) aligned with the sample surface normal and (B) 36° from the normal. Experimental data (solid circles), phason strain model (open squares), and Pauling twinning model (open triangles).

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Research was sponsored by the Division of Materials sciences, U.S. Department of Energy under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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Beamline Overview

The Oak Ridge National Laboratory (ORNL) beamline incorporates several novel design features which simplify the alignment and maximizes the flux available at the sample.¹ An important feature is a two-crystal monochromator which focuses the horizontal beam divergence with a dynamically bent Si(111) crystal in the sagittal focusing geometry.² Crystal focusing is attractive because it efficiently collects a much larger horizontal divergence than focusing with an X-ray mirror. In addition, sagittal crystal focusing allows for much better energy and momentum resolution than with a doubly focused mirror placed upstream of the monochromator which mixes twenty times as much horizontal into the vertical divergence. The advantages of crystal focusing outweigh the increase in operational complexity. We can continuously change from one X-ray energy to another, over several kilovolts, under computer control and maintain a focused beam. Another novel feature of the ORNL beamline is the use of a thermally stable and mechanically simple cantilevered mirror for focusing the vertical beam divergence.³ Details of the beamline performance are contained in ref. 1.

Experimental Program

During 1986 through March 1987, more than 25 experiments were performed on X14A. In general, these experiments were of materials science interest and suited to our beamline in terms of flux, energy resolution, and/or Q-space resolution. One of the big undertakings during the year was the measurement of the weak diffuse X-ray scattering from NiFe alloys. Although this data is still being analyzed, obvious size differences were found between the Ni and Fe atoms in the lattice. By tuning the radiation near an absorption edge, we are able to determine the pair interatomic vector. A measure of phason strain in Al_4Mn quasi-crystals was undertaken. This measurement shows a linear phason strain and rules out the Pauling icosotwin model. We undertook a study of the accommodation of strain at the nickel-sapphire interface and measurement of the surface roughness. The angular dependence of the real part of the anomalous scattering factors in a kinematically diffracting thin film of GaAs is under analysis. Further information can be obtained by writing to the principle authors.

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Research performed in part at the Oak Ridge National Laboratory Beamline X14 at the National Synchrotron Light Source, Brookhaven National Laboratory, supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, and under contract AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

A SIMPLE CANTILEVERED MIRROR FOR FOCUSING SYNCHROTRON RADIATION¹

G. E. Ice (ORNL) and C. J. Sparks (ORNL)

A large cantilevered mirror was constructed to focus the vertical divergence for the X14A beamline. The advantages of this mirror are its compactness, simple bending device, simplicity of construction, and good thermal contact to structures outside the vacuum. Details of the mirror and its performance are given in ref. 1.

The mirror figure was characterized prior to insertion into the beamline in June 1985, and its X-ray performance was carefully documented. It was then removed in March 1987, and the surface roughness and figure were measured. No degradation was found in mirror performance or surface after beam exposure.

The mirror reflectivity under various operating conditions was determined by monitoring the integrated flux through a 2.5 cm aperture sited 7 m from the mirror. The reflectivity at 8.333 keV and 6 mrad glancing angle was about 35%. The reflectivity was improved to 67% by going to a glancing angle of 3 mrad. This result is expected if surface roughness is responsible for the poor reflectivity. The estimated surface roughness from these measurements is from 21 to 26 Å.

A vertical focal spot size of 0.96 mm (4σ) was measured and compares to an ideal size of 0.61 mm based on our 1.5 magnification of the image of the electron beam. In the collimating mode a beam divergence of 1.8×10^{-4} (full-width, half-maximum) was obtained. By comparison, the opening angle of the source is about 4×10^{-4} rad, and the source size-limited divergence for a perfect collimating mirror located 7 m from the source is 6×10^{-5} rad.

After exposure to the unattenuated white radiation of the NSLS X-ray ring for approximately 6000 h, the mirror surface was measured and inspected for overall flatness with standard interferometric techniques. The mirror figure showed a mean radius of 10 km in the meridional plane which is removed during focusing by the application of a slightly greater bending moment. The figure error in the unbent mirror, however, may be responsible for the imperfect focusing properties. No degradation of the surface finish and no surface deposits were observed.

The rms roughness was measured by Takacs using a WYKO NCP 1000 5 mm profilometer. The surface roughness for spatial frequencies below 5 mm was found to range between 21 and 28 Å with most regions having about 24 Å rms roughness. This agrees well with the poor performance for the measured X-ray reflectivity. The mirror is being repolished to improve the surface figure and roughness.

One of the chief advantages of the cantilevered mirror is its thermal stability. Despite the fact that water-cooling channels in the mirror were not used, the mirror was found to be quite stable under varying beam currents. Figure 1 illustrates a long term stability of better than 0.38 eV or about 15 μrad. The iron K-edge was repeatedly scanned over a three-day interval with beam currents cycling between 50 and 200 mA.

¹ G. E. Ice and C. J. Sparks, "A Simple Cantilevered Mirror for Focusing Synchrotron Radiation," to be published in Nuclear Instruments and Methods.

Research performed in part at the Oak Ridge National Laboratory Beamline X14 at the National Synchrotron Light Source, Brookhaven National Laboratory, supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, and under contract AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

F . 1. The iron K-edge was scanned in energy over a period of three days to test the mechanical and thermal stability of the X-ray optics and the reproducibility of the electron orbit. Energy changes less than 0.38 eV were observed even though the beam current cycled between 50 and 200 mA.

STRUCTURAL STUDIES OF NICKEL FILMS AND THEIR INTERFACE WITH SAPPHIRE SUBSTRATES¹

C. J. Sparks (ORNL), M. Hasaka (Nagasaki U., Japan), D. S. Easton (ORNL), S. Baik (ORNL), T. Habenschuss (ORAU), and G. E. Ice (ORNL)

The structural perfection of epitaxial nickel films grown on the (00·1) or basal plane of heated sapphire (Al_2O_3) single crystals was studied with X-ray diffraction techniques. Nickel films approximately 700 Å thick formed by vapor deposition increased in perfection as the temperature of the sapphire approached 1400°C. Although the nearest nickel atom distances are 10.3% smaller than those of the closed-packed direction in sapphire, the strain was mostly accommodated at the interface rather than being distributed through the thickness of the nickel film. Diffuse rods of X-ray scattering which are associated with diffraction from the interface gave information that the interface was comparatively rough.

The orientation relationship between the nickel overlayers and the 00·1 deposition plane of sapphire was found to be $\text{Ni}(111)//\text{Al}_2\text{O}_3(00\cdot1)$ and $\text{Ni}\langle110\rangle//\text{Al}_2\text{O}_3\langle11\cdot0\rangle$. The nickel close-packed directions are parallel in the plane of the substrate. The atom spacing of bulk nickel in the $\langle110\rangle$ direction is 10.3% less than that of sapphire in the $\langle11\cdot0\rangle$ direction.

The penetrating depth of X rays permits studies of diffraction from interfaces buried even microns beneath the surface. Diffraction from multilayers is such an example. Studies of a single interface such as a grain boundary are known to give rise to measurable diffraction effects.² More recent work has shown that the abrupt termination of a crystal at a surface also gives rise to diffuse rods of X-ray scattering perpendicular to the surface.^{3,4} For a film thin enough to transmit the incident X-ray beam, the diffuse X-ray scattering from the nickel will include both the top surface and the interface with the substrate. The Al_2O_3 will produce X-ray scattering from its interface with the nickel film. We can separate the scattering associated with the nickel surface and interface from that of the sapphire interface by measuring those truncation rods containing either nickel- or sapphire-only reflections. Scans were made of the intensity distribution in the rods by making rocking curve measurements through them at various positions along their length. In particular, measurements were made near Bragg reflections where the interface scattering was most intense. Integrated intensities from such scans were corrected for background and for the Lorentz and polarization factors. These results for several truncation rods belonging to the Al_2O_3 and nickel reciprocal lattices are plotted in Fig. 1. A least squares fit to the data shows that the intensity fall-off follows the relation given by Andrews and Cowley:³ $\text{Intensity} = q_1^{-\eta}$, with η ranging between 2.63 to 2.78 for the Al_2O_3 interface and 2.6 for the nickel interface. Both the sharp and diffuse truncation rods predicted by Andrews and Cowley were observed for sapphire.³ That the nickel truncation rods were, for the most part, associated with the nickel-substrate interface and not the nickel surface was established by observing that roughening of the nickel surface with fine abrasive had no effect on the observed intensity. In addition, the known smoothness of properly prepared sapphire surfaces exceeds that expected for vapor-deposited surfaces. Theory for a sharp interface (a crystal terminated with a single atom plane as its surface) gives $\eta = 2.0$ [refs. 3 and 4]. Values of η may range up to four with four being associated with a very rough surface or interface.

Fig. 1. X-Ray intensity from Al_2O_3 and nickel overlayer interface plotted against q_1 is shown to vary as $q_1^{-\eta}$ where η approaches a value for a very rough interface.

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Research performed in part at the Oak Ridge National Laboratory Beamline X14 at the National Synchrotron Light Source, Brookhaven National Laboratory, supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, and under contract AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

MULTIPLE SCATTERING AND THE (200) REFLECTION IN SILICON AND GERMANIUM¹

J. Z. Tischler (ORNL), J. D. Budai (ORNL), G. E. Ice (ORNL), and A. Habenschuss (ORAU)

Recent indications of a possible nonzero structure factor for the silicon (200) reflection² pose an interesting question since, due to symmetry, the (200) X-ray structure factor (F) in diamond structure materials should be exactly zero.³ To investigate this question, we have made measurements of the (200) reflection in silicon and germanium. These measurements were placed on an absolute scale by using a PIN diode, one of the few devices with sufficient dynamic range to measure both a diffracting beam (10^3 counts/sec) and the direct beam (10^{10} counts/sec).⁴ The diffraction measurements were made at various azimuthal orientations. To properly determine $F(200)$, one must use dynamical theory and include the multiple scattering contributions of hundreds of nearby reciprocal lattice points.⁵ To simplify the computation of multiple beam rocking curves, it is convenient to use an approximation described previously.^{5,6} By measuring the absolute integrated intensity at various ϕ angles and comparing with calculations of the integrated intensity, one may determine the exact magnitude and phase of $F(200)$. We find that the measurements may be completely explained by multiple scattering with a (200) structure factor, $F(200)$, less than 0.0004 ± 0.00042 electrons for silicon and less than 0.00083 ± 0.00042 electrons for germanium. We conclude that previously reported sharp rocking curves measured at the (200) reflection are explained as multiple reflections.

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Fig. 1 Measured absolute integrated intensity shown as open circles with error bars from Ge(200) and Si(200) as a function of rotation, ϕ , about the [100] surface normal. The solid line is a theoretical calculation of the multiple scattering contribution from 400 beams and explains the observed intensity.

DEVELOPMENT AND USE OF A SIMPLE EXAFS SYSTEM ON A WHITE BEAMLINE (X-15A)

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The System

The EXAFS system consists of a channel-cut monochromator which accepts a white beam, an optical rail on which EXAFS accessories may be mounted, and a PC (ATT PC6300) and CAMAC crate to control the whole thing. The crystal is 220 Si, made from float-zoned, dislocation-free material. It is rotated by a Huber circle directly driven by a Compumotor microstepper. The optical elements currently used for EXAFS include a motorized slit, a PIN diode detector, an ion chamber, a photoelectron-yield chamber, and a fluorescence detector with shielding. The data are gathered by the PC via a CAMAC crate. Counting and timing are done in CAMAC, thus allowing counting to continue while keyboard commands are processed. The experiment-control program allows flexible control over the data-gathering process, as well as on-line data inspection during a scan. The output data format is that which feeds into the Bell Labs EXAFS analysis package, as implemented on PCs. This package is available on the PC.

Results

The above system produced Bell Labs' first full-range EXAFS spectra at NSLS, on Ni foil. After that, we then did EXAFS on quasicrystals, dilute solid solutions, and mechanical alloy systems.

T_2 Al-Li-Cu is one of two known stable quasicrystals. It can be obtained as rapid-quenched ribbon or as large-grain polycrystal. Close to it in the ternary diagram is a Frank-Casper phase referred to as R. It has been speculated that the quasicrystal and R structures are related. We performed photoelectron and fluorescence EXAFS measurements about the Cu edge in R and T_2 phases. We find that the Cu EXAFS from T_2 and R are almost identical, indicating a close structural relation between the two compounds. The R spectrum may be converted into the T_2 spectrum simply by attenuating the former by a factor of 0.88.

The alloy Al_3V may be quenched into a quasicrystal. In this system, there is no obvious model compound as there is in Al-Li-Cu or Al-Mn(-Si). The EXAFS pattern for this icosahedral phase is very different from that for Al-Mn. While the inferred RDF for Al about Mn is very broad, with two resolved peaks, that for Al about V is much narrower, again with two peaks. The EXAFS for i - Al_3V is surprisingly close to that for Al_3V , which is a simple tetragonal superstructure on fcc, with no obvious connection to anything icosahedral. The EXAFS evidence thus indicates that Al_3V is in a different structural class than Al-Mn(-Si).

Mechanical alloys are made by mixing powders of two or more elements together in a high-energy ball mill. The resulting compaction, fracture, and recompaction causes a mixing action which may extend down to the atomic level. Novel materials may be made this way. We have studied a 50-50 mixture of Cu and Fe at both the Cu and Fe edges. The Cu EXAFS remains fcc-like for all mill times, and the interatomic distance stays at $2.55\text{\AA}$. The Cu seems to be surrounded mostly by Cu neighbors. The Fe pattern evolves from bcc at the start to fcc-like at longer times. There are two distances about the Fe atoms, separated by $0.07\text{\AA}$. We conclude that the 50-50 alloy is a clustered fcc solid solution after long milling. Curiously, this alloy remains ferromagnetic, with a Curie point near 200°C . We also milled a 50-50 Cu-Nb mixture, in which the Cu remained fcc, while the Nb became disordered in a way we have not yet analyzed.

We have studied rapidly-quenched dilute alloys in which the solute atoms are much smaller than the solvent atoms. This mismatch induces insolubility in equilibrium, and interesting siting patterns when solubility is forced by rapid quenching. For instance, we find that 1% of Cu in Y yields an EXAFS pattern about Cu which shows two shells - disordered Y at $2.8\text{\AA}$ and disordered Cu at $2.52\text{\AA}$. We interpret this as due to disubstitutional siting of Cu in Y. We rule out the possibility that Cu has precipitated in the form of Cu-Y metallic glass (the most likely precipitate for this system) by comparing the spectrum for this glass with that of the dilute solution.

DEVELOPMENT AND USE OF A SIMPLE SAXS SYSTEM ON A WHITE BEAMLINE (X-15A)

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The System

The SAXS system consists of the monochromator and optical rail used in the BL X-15A EXAFS system (see other report), with a pinhole camera in place of the EXAFS equipment. The wavelength is set at $\text{CuK}\alpha$ using the EXAFS software. The pinhole camera consists of a collimator assembly and a He-filled flight path, which is about 25 cm long. The collimator is a pair of tube with brass plugs in the ends. The plugs have 1/2mm holes drilled in them to form the pinholes. For ease of alignment, there is a pair of wires cemented into the tube just after the first pinhole. These wires straddle the beam path and form a primitive ion chamber. The second plug has a heater and thermister in it, as well as a vertical hole for a 1mm sample capillaries. Thus, the second plug is the sample holder as well as the guard pinhole. Detection is photographic, using a screen-intensified polaroid Laue camera. A movable lead strip forms the beam stop. The main virtue of this system is compactness, as it measures less than 1m from beam port to camera.

The system easily resolves the scattering from Ludox, a suspension of $70\text{\AA}$ silica spheres in water. Lines down to $160\text{\AA}$ d -spacing should be visible. For typical liquid-crystal specimens, exposures of 5-30 min. are required.

Results

This system was intended for use with lyotropic and thermotropic phases, and has been used for such. For instance, we have measured the d -spacings for several alkylated sugars, and shown that the molecular packing is probably head-head interdigitated, as has been shown for other alkylated sugars. This result is relevant because it contradicts some work by others in which it was stated that the N-alkyl gluconamides were monolayer smectics, unlike all the others, which are bilayers. The N-alkyl gluconamides in their isotropic phases show fairly narrow rings of scattering, centered about the q value for the smectics. We interpret this as being due to remnant smectic order in the isotropic phase.

The surfactant AOT is known to show hexagonal, cubic, and lamellar phases when mixed with water. A commercial water solution of AOT is in the concentration range appropriate for the cubic phase, is optically isotropic as a cubic should be, but is much more fluid than a cubic made by adding water to purified AOT. We did SAXS on this preparation and find two diffuse rings of scattering instead of the several sharp ones others have found for cubic surfactant phases. We interpret this phase as being a disordered cubic, the disorder probably coming from impurities such as salts (known to be present) or hydrolysis products.

We see that even as primitive a system as described above is capable of useful diagnostic functions in liquid-crystal physics. Obvious upgrades, such as a position-sensitive detector, should greatly enhance the physics output.

INTERFACE STRUCTURE OF EPITAXIAL NiSi_2 ON $\text{Si}(111)$

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We investigated the interface structure of epitaxial layers of A-type and B-type NiSi_2 on $\text{Si}(111)$ with x-ray standing waves (XSW). The XSW results show that the Ni atoms at the interface are sevenfold coordinated i.e. the Si atoms of the silicide bond to the $\text{Si}(111)$ surface dangling bonds (compare figure 1a and b). Figure 2 shows the results of XSW measurements on four samples of different thickness.

Fig. 1 For A-type(a) NiSi_2 on $\text{Si}(111)$ all crystal axis align with the substrate whereas the cubic (CaF_2 -structure) epilayer is rotated by 180° around $\langle 111 \rangle$ in case of B-type(b). For CoSi_2 on $\text{Si}(111)$ the Co atoms of the epilayers are attached to the $\text{Si}(111)$ dangling bonds(c).

Fig. 2 Experimental results of the XSW measurements for four of the six investigated samples. Dots and circles represent the experimentally determined reflectivity and Co K_α fluorescence yield respectively. The solid curves are calculated according to the dynamical theory of x-ray diffraction and fitted to the experimental data.

The excellent crystalline quality of the NiSi_2 epilayers is reflected in coherent fractions which are as high as theoretically expected for perfect overlayers even for the 97.6 nm thick sample. From our results the interface distance Z_I (compare figure 1) is deduced together with the amount of interface relaxation ΔZ_I . Both types of NiSi_2 are relaxed inward, the A-type, however, more pronounced than the B-type.

Acknowledgments

We would like to thank B.M. Kincaid and J.B. Mock for valuable assistance at the AT&T beamline and J.R. Patel and P.E. Freeland for kindly lending us XSW instrumentation. This work was supported by the National Science Foundation under grant number DMR 8017 30303.

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INTERFACE STRUCTURE AND LATTICE MISMATCH OF EPITAXIAL CoSi_2 ON(111)

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We have used the X-ray Standing Wave technique and bulk X-ray diffraction to investigate the structural properties of thin CoSi_2 layers grown epitaxially on Si(111). The perpendicular lattice mismatch with respect to the Si substrate was found to be -0.0152 ± 0.0003 and -0.016 ± 0.001 for 6 nm and 16 nm thick layers respectively. The distance between Si(111) and the first Co layer was measured to be (0.288 ± 0.005) nm and is thus stretched by (0.014 ± 0.005) nm compared with a value determined by Si-like bond length. The Co atoms are attached to the Si(111) dangling bonds in agreement with the model of fivefold coordinated metal atoms at the interface.

Fig. 1 Simple models of the Si(111)/ CoSi_2 interface a) the cobalt atoms at the interface are attached to the Si(111) dangling bonds in a five-fold coordination. b) The Si atoms of the silicide are attached to the Si(111) surface leaving the Co atoms in the first layer sevenfold coordinated. The location of the Si(111) diffraction (lattice) planes which are located in the middle of the Si double layers is indicated. The substrate lattice plane spacing is denoted as d_{111} and the distance between the Si(111) surface and the first layer of cobalt atoms is z_I .

Acknowledgments

We would like to thank B.M. Kincaid and J.B. Mock for valuable assistance at the AT&T beamline and J.R. Patel and P.E. Freeland for kindly lending us XSW instrumentation. K.-G. Huang would like to thank W.M. Gibson for encouragement and his continued interest during this work. This work was supported by the National Science Foundation under grant number DMR 8017 30303.

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Fig. 2 Results of an XSW scan: + Experimental determined and --- fitted rocking curve, o experimental determined and — fitted Co K fluorescence yield. FWHM of the rocking curve is $35 \mu\text{rad} = 7.2 \text{ arcsec}$. The X-ray energy is E_γ .

As On Si(100) INVESTIGATED WITH X-RAY STANDING WAVES

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We used the X-ray Standing Wave (XSW) technique with Synchrotron Radiation to investigate the structure of monolayers of As on Si(100). Samples prepared in UHV had been provided with a protective coating of amorphous Si because the XSW measurements were performed outside of the UHV environment. The results of the measurements done at the X-15A AT&T Bell Labs beamline are in good agreement with the formation of As dimers. The model of As dimers as proposed recently by Uhrberg et. al.¹ is shown in Fig. 1. Each As bonds to two Si atoms and to a neighboring As atom, is thus threefold coordinated and electronically left with a doubly occupied lone-pair state. This model was mainly supported by pseudopotential calculations and angular resolved photoemission. The present XSW study yields structural information by determining the distance Z_I between the As overlayer and the ideal Si(100) surface (compare Fig. 1b). The result of an XSW measurement is shown in Fig. 2.

Fig. 1 As dimers on the Si(100) surface in top view (a) and side view (b). The size of the (100), 1x1 surface unit cell is $d_{110} \times d_{1\bar{1}0}$. The size of the 2x1 surface unit cell of the dimers is $2d_{110} \times d_{1\bar{1}0}$. This simplified model shows only one type of domain of As on Si(100), ($d_{100} = a_{Si} = 0.357$ nm, $d_{110} = a_{Si}/\sqrt{2} = 0.253$ nm). The As saturation coverage is 1 ML.

Fig. 2 Result of an XSW on an unprotected Si(100)-As sample. The experimentally determined (+) and fitted (---) reflectivity as well as the experimentally determined As K_α fluorescence (0) and the fitted fluorescence yield (—) are plotted as a function of Bragg angle.

The distance of the As dimers normal to the ideal (100) surface was found to be (0.126 ± 0.001) nm which agrees well with the distance $Z_I = 0.132$ nm deduced from the pseudopotential calculations. Without a protective coating the As position was influenced by the surrounding atmosphere. However, the As phase formed under these circumstances appeared to be surprisingly stable.

¹R.I.G. Uhrberg, R.D. Bringans, R.Z. Bachrach, J.E. Norethrup, Phys. Rev. Lett. 56, 520 (1986).

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A SOFT-HARD X-RAY BEAMLINE FOR PHOTOABSORPTION, PHOTOEMISSION, AND STANDING WAVE MEASUREMENTS IN THE ENERGY RANGE OF 0.5-15 keV

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A versatile, focused, ultra-high vacuum beamline has been completed this year for performing combined electronic and geometric structural measurements of bulk, interface, and surface species. The basic layout of the design is source + collimating premirror + monochromator + focusing mirror + experiment. A variety of problems inherent with previous designs have been minimized or eliminated and a number of desirable features have been expanded. The table below summarizes these features.

Feature	Achieved By
1. High energy resolution	<ul style="list-style-type: none"> • variably bent collimating premirror • post-monochromator location of focusing mirror
2. Wide energy range	<ul style="list-style-type: none"> • rapid exchange of several different premounted crystal pairs (involves venting vacuum-isolated, differentially-pumped monochromator; 30 min. total turnaround time). • UHV beamline — no Be windows • <7 mrad incident angle on focusing mirror
3. High beam stability	<ul style="list-style-type: none"> • air-cooled rotatable premirror (decreasing heat load on first monochromator crystal) • water-cooled first monochromator crystal, thermally coupled with liquid gallium • multi-feedback, position-sensitive I₀ system • vibrational isolation of mirrors • improved, robust, fixed-exit monochromator design
4. High beam brightness	<ul style="list-style-type: none"> • low surface roughness, excellent figures of Pt-coated electroless Ni-on-Al mirrors (cylindrically bent flat ≈ paraboloid; cylindrically bent cylinder ≈ toroid) • independent, variable vertical focusing of two mirrors • reliable mirror bending mechanism
5. High beam purity	<ul style="list-style-type: none"> • low-pass filter: variable grazing incidence angle on premirror, 0-28 mrad, cutting out higher harmonics (entire beamline rotates to follow reflected beam) • high-pass filter: various absorbing films available—0.4 μ C, 1.6 μ C, 1.6 μ Al, 240 μ Be
6. Ultra-high vacuum	<ul style="list-style-type: none"> • differential pumping in long (9m) drift tube ensures true UHV (<10⁻¹⁰ Torr) in experiment
7. Variable focus at experiment	<ul style="list-style-type: none"> • easy to change incidence angle on post-monochromator focussing mirror • two sequential in-line experimental stations planned, operating in either/or mode

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DIRECT SCATTERING STUDIES OF THE MELTING OF LEAD SURFACES

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Of fundamental importance in understanding melting of three-dimensional crystals is the simple question: Do surfaces melt at a lower temperature than the bulk equilibrium melting temperature (T_m)? The presence of surface melting at low temperatures (premelting) has been invoked to explain the lack of superheating during melting and is consistent with simple intuition regarding vibrations at surfaces. A wide range of theoretical and molecular dynamics simulations have predicted that surfaces do in fact melt below T_m . Experimentally, ion channeling results suggest that the Pb(110) surface melts at up to 50°K below the Pb melting temperature of 600°K and that up to 20 molten layers are present on the surface at temperatures very close to the melting temperature [1] [2]. However, these studies do not yield a direct measurement of liquid correlations on crystalline surfaces and are only indirect evidence for premelting.

Figure 1 shows radial scans along the (110) azimuth from the Pb (110) surface for various temperatures. As is clearly seen, a strong diffuse component appears at momentum transfers of $2\text{\AA}^{-1}$ and $4\text{\AA}^{-1}$ as the temperature is increased from 380°K to 597°K. Azimuthal scans (rotation about the surface normal at constant momentum transfer) are shown in the inset and demonstrate that these peaks in the diffuse spectrum are also rotationally diffuse. We emphasize that these are rings in reciprocal space and are not diffuse streaks connecting Bragg points.

Figure 2 shows the integrated intensity of the $2\text{\AA}^{-1}$ peak as a function of temperature. The average scattering intensity from the (110) surface (at 599°K) is ≈ 100 photons/sec and corresponds to ≈ 3 layers of liquid on the surface. Figure 2 also shows the integrated intensity from the (111) surface as a

function of temperature. We calculate that there is $< \frac{1}{2}$ monolayer of liquid on the (111) surface at 1° below T_m .

In summary, we observe diffuse scattering from liquid layers on the Pb (110) and (111) surfaces at temperatures substantially below the bulk melting point of Pb. Surprisingly, the initial liquid scattering appears at $\approx 230^\circ\text{K}$ or $< \frac{1}{2} T_m$ on both the (110) and the (111) surfaces. On the (110) surface,

analysis of the scattered intensity yields 2-3 monolayers of liquid from 575°K to 599°K while substantially less than 1 monolayer of liquid is present on the (111) surface.

We would like to thank W. K. Waskiewicz for his extraordinary efforts in commissioning X16A and G. Wright for his assistance.

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VERTICAL STRUCTURAL INVESTIGATION OF Au(110) 1x2

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There are two reasons for further work on this surface: unresolved questions about the out-of-plane structure, and its interesting temperature dependence. Previous work using a rotating anode source demonstrated a missing row model of the reconstruction but with uniaxial disorder which was found to depend on annealing time and conditions. Roughening is also expected to take place on this surface at relatively low temperatures. We did a preliminary investigation of both aspects of the problem, which is well suited to our *in-situ* UHV system.

We observed abrupt ordering of the 1x2 phase at 200° and the gradual disappearance of the half-order intensity associated with the phase transition at 400°C. Under no circumstances of preparation were we able to obtain coherence lengths better than 150Å in the surface [100] direction corresponding to the disorder.

We measured the perpendicular momentum transfer dependence of the integrated diffraction intensity along several half-order rods. The figure below shows an example. In several cases we observed nodes in the curves and in general there was much more structure along the rods than we expected from a reconstruction involving just the three topmost layers. Furthermore the position of the nodes was found to change slightly with preparation conditions and was always different for the [100] and [100] directions. We know that our sample was miscut in this direction, and that there must be many steps within the coherence length. We expect that the curves can be explained as interference between ordered regions at different heights that arise from the steps.

DIFFRACTION STUDIES OF TE OVERLAYERS ON CU(100)

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We sought to investigate the ordering of fractional monolayers of a strongly bound element upon a simple substrate. We found an ordered $p2 \times 2$ phase at around $1/4$ monolayer Te coverage which was stable up to about 200°C . We obtained a surface x-ray diffraction signal of 3000 c/s in the $(1/2, 1/2, 0)$ peak and observed its temperature dependence as shown below. The phase transition is broad but has some hysteresis. We believe the hysteresis to be a problem with the thermocouple.

We measured a full set of 17 surface diffraction intensities along with symmetry equivalents for the annealed $p2 \times 2$ state at room temperature. We expected a trivial structure with one atom per unit cell. This would have a diffraction pattern with all intensities equal, except for smooth form- and Debye-Waller-factor effects. To our surprise we found a systematic pattern with half orders stronger than integer orders stronger than truncation rods. The indexing was the same as for bulk Cu. The suppression of the truncation rods was expected because Te is approximately twice as heavy as Cu, but the other difference was not. Subsequent analysis has shown that this is due to disorder in the overlayer, which gives rise to partial (20%) occupation of secondary sites in the $p2 \times 2$ unit cell. It is expected that this will correlate with the linewidths of the peaks which indicate a domain-wall disorder.

STRUCTURAL ANALYSIS OF Si(111)7×7

I. K. Robinson, W. K. Waskiewicz, P. H. Fuoss, and L. J. Norton (AT&T Bell Laboratories)

This was the first experiment performed on X16A and so was intended as a benchmark of surface x-ray diffraction. We had run Si(111) 7×7 at SSRL and so could make a performance comparison.

X16A is customised for diffraction experiments in UHV. It has a toroidal quartz, Pt coated mirror which accepts 3.5 mrad of light at 5.67 mrad incidence angle. This is monochromated by a double crystal Si(111) monochromator built by Princeton Research Instruments. A UHV system sits inside the hutch at the focal point. The sample is prepared by standard methods (here sputtering and annealing) and then transferred onto the centre of the 4 axes of an external Huber diffractometer which couples to the UHV system by bellows and rotary seal. A scintillation detector sits behind the resolution-defining slit on the 2θ arm.

Intensity data were collected by ω-scans of which a typical result is shown top left in the figure. The sample is inclined using the X-motion until the incident and diffracted beam were around 0.5° to the surface. By staying above the critical angle for total reflection, we avoid refraction complications but can still take advantage of the improved signal to background and favourable resolution function of the grazing incidence geometry. We used a 2x10 mm detector slit at 0.5 m which accepts a 1° range of exit angles. Because of the smaller beam size we illuminated a quarter of the sample area compared with the equivalent setup at SSRL, yet we obtained 70% of the signal rate obtained on the wiggler beamline VII-2 end station there.

Measurement on Si(111) 7×7	SSRL VII-2	NSLS X16A
(1, 0, 0.06) truncation rod	1280 c/s	733 c/s
(1, 3/7, 0.12) surface peak	218 c/s	167 c/s

The intensities of at least three symmetry equivalents of each surface peak were measured and averaged together to obtain error bars. The reproducibility of the data was 15% in intensity for strong reflection and greater (because of statistics) for weak ones; a compound error was thus derived. The measured data are shown as the areas of the left half circles in the figure. The right half circles were calculated for a model derived from that of Takayanagi after refinement of all the atomic coordinates. The result shows the presence of strain fields in the surface.

POLARIZATION ANALYSIS OF MAGNETIC X-RAY SCATTERING

D. R. Harshman and D. B. McWhan (AT&T Bell Labs) and D. Gibbs (BNL, Upton)

On beamline X16B the degree of circular polarization can be changed by translating the premonochromator slit normal to the plane of the synchrotron. The components of the linear polarization of the scattered beam are measured using an analyzer crystal with a scattering angle, two-theta, of 90 degrees. The x-ray energy was chosen so that two-theta for the graphite (006) was 90 degrees. A polarization analyzer has been built in which the graphite crystal can be rocked in both directions under stepping motor control and also rotated around the scattered beam. In this way integrated intensities for the two components of polarization can be measured. The efficiency of the polarization analyzer is illustrated in fig. 1. This shows the intensity as a function of the angle of rotation of the analyzer.

The polarization of the x-ray beam from a bending magnet is strictly linear in the plane of the electron orbit and becomes increasingly right or left elliptically polarized above or below the plane. The degree of linear polarization, defined as $(I(\text{perp.}) - I(\text{parallel})) / (I(\text{perp.}) + I(\text{parallel}))$, versus the vertical displacement of the premonochromator slit on X16B are shown in fig. 2. The measurements were made on the (200) reflection from an iron film, and the component of polarization parallel to the scattering plane was corrected for the $\cos^2(2\theta)$ dependence of charge scattering. Similar measurements have been made at DESY (1) and LURE (2) with comparable results.

In magnetic x-ray scattering, the orbital and spin densities of a magnetically ordered material can be separated from an analysis of the polarization of the scattered beam (3,4). For a simple basal plane spiral antiferromagnet the separation can be made using a linearly polarized incident beam. For a basal plane ferromagnet, it is necessary to compare the flipping ratios for both right and left circularly polarized incident beams (2). We have made preliminary measurements on the antiferromagnetic spiral structure of holmium metal. With an incident flux of 2×10^{10} photons/sec on the sample the intensity of the (004)+ pure magnetic peak was ~400 counts/second before polarization analysis and ~4 and ~20 counts/second after scattering from the analyzer in the directions perpendicular and parallel to the scattering plane respectively. These results show that polarization analysis of magnetic scattering is feasible on a bending magnetic source.

Fig. 1 Intensity vs analyzer angle for the polarization analyzer with 0° corresponding to polarization perpendicular to the scattering plane and 90° in the scattering plane.

Fig. 2 Degree of linear polarization vs vertical displacement from the orbit on X16B.

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The simplest interface one can conceive is an atomically smooth facet, separating a crystalline element from its vapor. However, a recurrent idea of the last thirty years is that of a surface roughening transition¹, which may occur at a much lower temperature than bulk melting. Below the roughening temperature (T_R), the interface corresponds to the ideal, but for $T > T_R$, its behavior is determined by surface stiffness. There have been few experimental studies of the microscopic aspects of interfacial roughening.

Here, I report the results of an x-ray diffraction study of the (110) face of copper, between 200° C and 700° C. A longer report of this work has previously appeared.² From the T dependence of the Bragg reflectivity, $T_R \approx 600^\circ$ C is deduced. This provides the first direct observation of a roughening transition of a low-index face of a metal crystal. The choice of copper was motivated in part by studies of the equilibrium crystal shape (ECS) of 5 μ m metal crystals^{3,4}, close to their melting temperatures. Specifically, it is known that the (110) face of copper is absent from the ECS immediately below its melting temperature ($T_m = 1083^\circ$ C)⁴, implying that this facet has already roughened. In addition, the diffraction measurements of Lapoujoula et al. suggest that the (113), (115) and (117) faces undergo roughening transitions.⁵ One advantage of x-ray diffraction is that behavior on length scales between 1 Å and 1 μ m is accessible.

These measurements were performed on X16B, using a Ce (111) monochromator, bent to focus 2 mrad. of synchrotron radiation into a spot 0.5mmX5mm at the sample position. A high resolution configuration utilized a Ge (111) analyzing crystal. The sample was cut to expose the (110) face and then Syton polished. Fig. 1 shows profiles at several temperatures near (001). For an f.c.c. structure there is no Bragg peak at (001). These data correspond to scans transverse to the reflectivity which extends between the (111) and the (111) Bragg peaks.⁶ The (001) position is particularly sensitive to surface roughness, because successive planes scatter out of phase. Importantly, the profiles are close to the resolution limit, with a FWHM of 0.0008 Å⁻¹, implying that the surface is well-defined over lengths of >0.5 μ m. Also, there is no increase in width with increasing temperature. However, diffuse scattering away from the Bragg reflectivity cannot be ruled out. The behavior is quite reversible - the intensity remains nearly constant between $T = 200^\circ$ C and $T = 350^\circ$ C, but decreases upon further heating. By nearly $T = 600^\circ$ C, the intensity has fallen to zero - much more rapidly than can be accounted for by a simple Debye-Waller factor. At this temperature, there are numerous atomic steps on the (110) facet. This is precisely the requirement for a roughening transition. Thus, I tentatively identify $T_R \approx 600^\circ$ C. Strictly, this is a lower bound on T_R .

Fig. 1 Scans transverse to the Bragg reflectivity at (001). The solid lines are all the same shape. The change in peak position is a result of thermal expansion.

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I thank B. Larson and J. Budai for the sample and B. Flood for preparing it. G. Wright provided excellent technical assistance. I have enjoyed discussions of this work with D. Gibbs, D. McWhan, and I. Robinson. I am grateful to everyone involved in the development of the AT&T beam lines, especially D. McWhan and B. Buntschuh for their collaboration on X16B.

ISOTOPE EFFECT ON THE MELTING TEMPERATURE OF NON-POLAR POLYMERS

F. S. Bates, H. D. Keith, and D. B. McWhan (AT&T Bell Labs)

The isomorphous monoclinic-(011) forms of "normal" (hydrogenated) and perdeuterated hexatriacontanes ($n\text{-C}_{36}\text{H}_{74}$ and $n\text{-C}_{36}\text{D}_{74}$) have been examined by X-ray diffraction at room temperature. Substitution of deuterium for hydrogen results in slight reduction in the parameters $a_s = a \sin \beta$ and b of the orthorhombic subcell by $0.33 \pm 0.02\%$ and $0.19 \pm 0.02\%$ respectively (within experimental error the c parameter appears to be unaffected). This reduction in cross sectional area of the unit cell as seen in projection along the chain axis is primarily a consequence of C-D bonds being slightly shorter than C-H bonds. Based upon the change in molecular volume, and an associated change in molecular polarizability, a relationship is proposed to account for the difference in melting temperatures of normal and perdeuterated hexatriacontane. This relationship also predicts successfully corresponding differences in melting temperature occasioned by perdeuteration of polyethylene and isotactic polystyrene, but fails to do so in the case of isotactic polypropylene. We speculate that, in the latter case, isotope substitution influences rotational degrees of freedom of pendant methyl groups, leading to an isotope dependent entropy of melting not experienced in the other species cited.

HOT PHONONS IN QUARTZ

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We have performed a time-resolved x-ray diffraction study of non-equilibrium phonons in α -quartz at low temperatures where the phonon generation mechanism is direct stimulation of TO phonons by infrared light excitation using a powerful CO₂ laser. For the initial phonon generation we have used the fact that the intense 10.6 μm CO₂ laser line very nearly matches the TO phonon induced infrared absorption in α -quartz near 9.38 μm . The lifetime broadening of this TO mode excitation is so large that there is significant population of this mode even though there is a frequency mismatch. While there is no hope of observing the lifetimes ($t \sim 1$ fs) of the optical phonons, we performed the experiment in a time-resolved manner in order to distinguish the resulting LA and TA modes arising from the initial laser pulse as these phonons propagate through the sample. This also allowed us to measure the steady state thermal diffuse scattering since scattering was measured prior to the firing of the laser.

The experimental setup is shown in Fig. 1. The sample material was synthetic quartz whose orientation was determined by Laue photographs. The x-rays used in this experiment were synchrotron radiation monochromatized to an energy of 15.08 KeV. The x-ray beam which struck the sample was about 0.5 mm high $\times$ 2 mm wide. The sample was mounted in a CTI refrigerator which was then mounted on the χ ring of a four circle Huber diffractometer. The CO₂ laser was Q switched by a mechanical chopper at a frequency of 10,000 Hz, with a pulse width of 200 nsec and a peak power of 10 KW.

A timing signal was derived from the laser pulse by collecting the outer ring from the laser TEM₀₁ mode onto a photon drag detector. This signal, which was delayed by ~ 1 μsec from the detector's output, was used to start the time-resolving data acquisition system. The x-rays scattered by the sample were collected by a Harshaw NaI(Tl) scintillation detector. The output of the scintillation detector was delayed by 4 μsec to ensure that x-rays which were scattered by the sample before and during the laser pulse could be collected by the time-resolving module.

Typical experimental results are shown in Fig. 2. This figure shows the diffuse scattering at (0.0.1.9), near the Brillouin zone center. The x-rays strike a region of the sample approximately 2.0 mm from the top, where the laser impinges. The diffuse scattering has been normalized for monitor counts and laser pulses. The baseline approximates the thermal diffuse scattering with no laser striking the sample.

The laser pulse is indicated striking the sample at $t = 0$. Shown are the calculated arrival times of (001) propagating TA and LA phonons at a point 2.0 mm from the top of the sample after being generated, presumably, by TO phonons created by the laser at the top of the sample. Arrival times for phonons reflecting off the bottom of the sample are included. In this range of phonon wavevectors, the x-ray diffuse scattering will be sensitive to the nearly stationary optical phonons and the acoustic phonons propagating with the acoustic sound velocity.

There is consistently a peak at the time corresponding to the firing of the laser. This confirms the existence of non-equilibrium (hot) phonons in the quartz. The fact that they are non-equilibrium and not thermal was confirmed in another experiment.¹ The first peak in the diffuse scattering data is consistent with the arrival times of acoustic phonons generated at or near the surface. Other peaks in the diffuse scattering data occurring somewhat later (> 2 μsec) do not seem to match transits of the acoustic phonons. These peaks could be due to the slowly propagating optic modes.

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Research performed at MATRIX beamline X-18A and supported by DOE contracts DE-FG02-85ER45183 and DE-AC02-76CH00016.

Figure 1

Figure 2

STRUCTURE AND PHASE TRANSITIONS OF HEXANE MONOLAYERS ADSORBED ON GRAPHITE

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Hexane monolayers adsorbed on a graphite basal plane surface exhibit interesting structures and phase transitions which we have been investigating by synchrotron x ray diffraction. Our attention was drawn to this system by neutron scattering experiments at the University of Missouri Research Reactor which indicated unusual melting behavior of the commensurate monolayer to a highly-correlated fluid phase. The rod-like shape of the hexane molecule suggested to us that the monolayer fluid might be a liquid crystal.

Fig. 1. Projection on the graphite (0001) surface of the unit cell for the commensurate monolayer phase of C_6D_{14} .

From our neutron and x ray experiments, we infer the commensurate ($2 \times 4\sqrt{3}$) herringbone structure shown in Fig. 1 for a complete monolayer of deuterated hexane (C_6D_{14}) adsorbed on exfoliated graphite at 10 K. The herringbone arrangement is similar to that found for other nonspherical molecules on the graphite (0001) surface.

In a series of measurements at the MATRIX beam line (X18A) in December, 1986, we observed the temperature dependence of the x ray diffraction patterns from a ~1.5-layer hexane sample shown in Fig. 2. The patterns at 6 K and 130 K can be explained by the coexistence of a complete commensurate monolayer with bulk hexane. The asymmetric peaks marked (M) have the characteristic Warren lineshape expected for a polycrystalline monolayer. The broader, symmetric peaks marked (B) are at the positions predicted for the bulk solid, while the peak labeled (?) appears to be an artifact of imperfect background subtraction.

The bulk diffraction peaks in Fig. 2 disappear by 175 K, i.e., below the melting point of bulk hexane at 178 K. We are tentatively interpreting this behavior as evidence of a layering transition in which a second layer of film (possibly fluid or amorphous) forms at the expense of bulk. Above 175 K, the Bragg peaks of the commensurate monolayer begin to broaden, disappearing near 190 K. It is quite unusual for the melting point of a physisorbed film to exceed that of bulk. In the case of hexane, we attribute it to steric hindrance of the rod-shaped molecule to rotational motion about a surface normal. A broad peak remains in the diffraction patterns above 190 K, although it appears weaker than in the neutron experiments. Whether this results from a liquid-crystal-like phase will require further measurements of the peak lineshape as a function of temperature. In conjunction with these experiments, molecular dynamics simulations of the melting of hexane monolayers on graphite are now in progress by F.Y. Hansen at The Technical University of Denmark.

Fig. 2. X ray diffraction from ~1.5 layers of C_6D_{14} adsorbed on a graphite foam substrate.

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²H. Taub, in The Time Domain in Surface and Structural Dynamics, NATO ASI Series, edited by G.J. Long and F. Grandjean (Reidel, Dordrecht, 1983).

This work was supported by NSF Grants DMR-8304366 and DMR-8704938, Israel-U.S. Binational Science Foundation Grants No. 2687 and 86-00294, and the MATRIX PRT by DOE Grant No. DE-FG02-85ER45183.

SOLUTION OF THE PHASE PROBLEM IN CRYSTALLOGRAPHY BY MULTIPLE BRAGG SCATTERING. Q. Shen and R. Colella (Purdue U.).—Multi-beam diffraction, in conjunction with the notion of Virtual Bragg Scattering (VBS), has been proved to be a feasible method for determining phases of structure factors in diffraction experiments. A VBS situation is one in which a weak "main" reflection (hkl) is fully excited, and another simultaneous strong reflection (HKL) is weakly excited by a suitable choice of the azimuthal angle ϕ around the scattering vector G_{hkl} . The asymmetric pattern obtained as the crystal is rotated around G_{hkl} is used to extract phase information. While encouraging results were obtained on perfect (Ge,Si) and mosaic inorganic crystals (V_3Si), some problems and limitations of the method were encountered with molecular crystals, because their reciprocal space is densely populated, and their nodes (Bragg reflections) have very small sizes on account of the small values of the structure factors involved. We report here on a recent experiment performed at NSLS (Brookhaven National Laboratory) that successfully revealed the phase related asymmetry effect on the (202) reflection of a large, parallel sided, organic crystal (benzil: $C_{14}H_{10}O_2$), by utilizing 3.5 keV soft x-ray radiation. A multi-beam calculation with mosaic spread included shows good agreement with the experimental data. Further analysis indicates that it is possible to extract arbitrary values of the phase angle from an experiment, for a noncentrosymmetric crystal, by using an analytical formula derived from a perturbation theory of the asymmetry effects. The same experiment was repeated at SSRL using a small quasi spherical crystal (diameter ≈ 0.3 mm) and the same result was obtained. It is now clear that our method, based on the notion of Virtual Bragg Scattering, can be applied to any kind of crystal with arbitrary shape. This work was supported by NSF.

PHASON DISPERSION CURVES IN TANTALUM DISULPHIDE BY X-RAY SCATTERING. W. Minor, L. D. Chapman, S. N. Ehrlich and R. Colella (Physics Department, Purdue Univ.).—The thermal diffuse x-ray scattering in the neighborhood of first order satellites has been measured with high resolution in $1T_1$ -TaS₂ (incommensurate phase), using synchrotron x-rays at NSLS ($\lambda=0.711$ Å). A total of about 2400 points in q -space have been measured at 363 and 423 K in small "boxes" surrounding two first order satellites, one close to (010) and the other one close to (030). Our analysis shows that Phason Diffuse Scattering (PDS) falls off like q^{-2} , and that the iso-diffusion surfaces surrounding a satellite reflection are ellipsoids, reflecting the anisotropy of PDS as predicted by theory¹. For a satellite whose projection on the $hk0$ plane is located along the $\vec{b}^*$ axis, the largest ellipsoidal axis is parallel to $\vec{c}^*$, and the shortest one is parallel to $\vec{b}^*$. The ratios of the three axes are 2.5, 1.8, 1. Absolute measurements of the scattered intensity have led to a quantitative determination of the phason velocities (v_p 's) in various directions. The value of v_p along $\vec{b}^*$ is about 1.3×10^5 cm/sec, while along $\vec{c}^*$ the velocity v_p is about 1/3 smaller (4.7×10^4 cm/sec). As the temperature is increased from 363 to 423 K, the velocity along $\vec{b}^*$ is essentially unchanged, but along $\vec{c}^*$ the value of v_p is decreased by 13 % approximately. This work is one of the first examples of a fully determined phason spectrum. This work was supported by MRL-NSF.

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STRUCTURAL DETERMINATION OF THE TiO_2 (100) 1×3 RECONSTRUCTED SURFACE

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Introduction

The catalytic and chemisorption properties of metal catalysts supported on oxides such as TiO_2 are to some extent affected by the nature and properties of the substrate. Such is the behavior of the so called strong metal-support interaction, SMSI. The clean, ordered (100) surface of rutile TiO_2 is known to reconstruct to form a 1×3 , 1×5 , or 1×7 LEED image, determined by the annealing temperature. The aim of this investigation is to locate the atomic coordinates of the 1×3 surface by using the glancing angle diffraction (GAD) technique. Additionally, complementary LEED data, taken at normal incidence, is collected from the same surface.

Experimental Description

The experiment was performed at beamline X-18A, operated by the MATRIX PRT, and used a transportable, ultra-high vacuum (UHV) chamber developed for surface and interfacial diffraction studies. This chamber mounts directly to a Huber 4-circle diffractometer, and permits glancing angle incidence through a 0.015" thick cylindrical Be window. In-situ preparation of the surface of interest is possible since a transfer cell is not used, and vacuum integrity can be maintained throughout the experiment. The preparation features provided include Ar^+ ion sputter cleaning, and annealing to temperatures in excess of 600°C . And diagnostic capabilities include retarding field Auger electron spectroscopy, as well as pulse counting LEED. The pulse counting LEED allows for quantitative data collection by storing LEED images in computer memory. A series of images is collected, and can be used to obtain comparisons with theoretical calculations for one or more LEED peaks. So, LEED and GAD data are collected from the same structure.

Results

It has been verified that the surface diffraction chamber can be used successfully for GAD and LEED data collection from the same 1×3 surface reconstruction. In this study, 20 unique surface reflections were measured with GAD. Figure 1 shows the results of several scans of one such surface peak, taken over a period of several days.

Figure 1: Several rocking curve scans of a surface peak.

The stability of the surface is seen to be good, and the peak intensity reliably reproducible. While at this time no conclusions can be stated with regard to the structural determination, analysis of the x-ray and LEED data is not complete. It is anticipated that upon completion of analysis and refinement, a structural determination will result.

This work was supported, through the MATRIX PRT, by the U.S. DOE under grant No. DE-FG02-85-ER45183.

MOLECULARLY ORDERED ELECTROPOLYMERIZED FILMS OF $[\text{Ru}(\text{v-bpy})_3]^{+2}$: AN X-RAY STANDING WAVE STUDY¹

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The preparation and characterization of well defined microstructures on electrode surfaces are areas of active research since such engineered structures have been shown to exhibit novel and interesting properties.[1] A particularly exciting possibility would be the preparation of films that are ordered down to molecular or atomic dimensions since this would allow the development of molecularly organized devices. Given that electropolymerization of transition metal complexes containing vinyl-substituted ligands [2] (e.g. vinyl-bipyridine and related materials) is a very versatile technique for the deposition of very thin films of electrochemically active polymers, we have investigated the possibility of employing such a technique for the deposition of molecularly thin and ordered polymeric films of the monomer complexes. In order to ascertain the degree of order of such deposited films, we have employed the x-ray standing wave technique (XSW) since it represents an extremely sensitive tool for determining the position of impurity atoms within a crystal or adsorbed onto crystal surfaces.[3] One of the problems associated with the implementation of the standing wave technique is that it requires the use of perfect or nearly perfect crystals. An alternative is the use of synthetic layered microstructures (LSM) and we recently reported a study on the use of LSM in the investigation of electrochemical interfaces.[4] We now present some preliminary results on the deposition of molecularly ordered films of $[\text{Ru}(\text{v-bpy})_3]^{+2}$ on a tungsten carbon LSM.

$[\text{Ru}(\text{v-bpy})_3]^{+2}$ was prepared and electropolymerized, as previously described,[3] on a W/C LSM (Energy Conversion Devices) employed as an electrode and consisting of 200 layer pairs of tungsten and carbon of 6 and 24 Å thick each, respectively and with tungsten as the outermost layer. Integration of the area under the voltammetric wave gave a coverage of about 5 monolayers. After deposition, the electrode (LSM) was rinsed with acetone and mounted on a Huber model 410 goniometer stage providing better than 10 microradian angular resolution. All experiments were performed at the X-18B beam line of the National Synchrotron Light Source at Brookhaven National Laboratory. Monochromatic radiation at 22.5 keV was obtained with a Si(220) double crystal monochromator with 50% detuning to eliminate higher harmonics. Both the reflectivity and the $\text{RuK}\alpha$ fluorescence intensity curves were obtained simultaneously as the angle of incidence of the x-ray, relative to the electrode surface, was scanned across the first order Bragg reflection peak. A reflectivity scan of the unmodified LSM showed a well

Figure 1. Characteristic $\text{RuK}\alpha$ fluorescence at 19.3 keV (A) and reflectivity curve (B) for a W/C LSM modified with an electropolymerized film of $[\text{Ru}(\text{v-bpy})_3]^{+2}$. Incident x-ray energy was 22.5 keV.

developed first order Bragg reflection with a reflectivity maximum at about 9.7 milliradians which correlates well with the calculated value of 9.3 milliradians for an incident energy of 22.5 keV and a 30 Å d-spacing. The difference in the values more than likely arises from having a d-spacing slightly different from 30 Å.

The LSM was modified with a polymeric film of $[\text{Ru}(\text{v-bpy})_3]^{+2}$ as described above and again analyzed via the XSW technique. The incident energy (22.5 keV) was such that characteristic $\text{RuK}\alpha$ (RuK edge is at 22.1 keV) fluorescence at 19.3 keV could be excited so that both the reflectivity and the fluorescence intensity could be simultaneously monitored. Figures 1A and B show the angular dependences of the $\text{RuK}\alpha$ fluorescence intensity and the reflectivity of the W/C LSM, respectively. The reflectivity curve (Fig. 1B) is essentially identical to that obtained prior to modification, indicating that the properties of the LSM were unaltered by the polymer electrodeposition. Figure 1A shows the angular dependence of the $\text{RuK}\alpha$ fluorescence and although the data is rather noisy, there is a well defined modulation. The fluorescence intensity peaks on the low angle side of the reflectivity curve and then decreases as the angle is advanced through the first order Bragg reflection. The sole fact that a modulation is observed is a clear indication that there is order, down to atomic dimensions, in the deposited layer. The general shape of the modulation indicates that on the average, the ruthenium centers are closer to the midpoint between diffracting planes than to the diffracting planes themselves (actually, the projection of these planes away from the interface). In conclusion, we have shown that simple electrochemical techniques can be employed in the preparation of molecularly ordered layers and that these can be characterized with the x-ray standing wave technique. We are currently investigating the preparation of segregated layers of these polymers and preliminary results indicate that these also retain their order. In addition we are also investigating the diffracting properties of these films.

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¹This work was generously supported by the Materials Science Center at Cornell University, the National Science Foundation, and the Army Research Office. HDA is a recipient of a Presidential Young Investigator Award and an A. P. Sloan Fellow.

NEAR TOTAL EXTERNAL FLUORESCENCE FROM Mn-STEARATE MONOLAYER

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The adsorption of a metal ion from the subphase solution to the liquid-air interface, induced by a surfactant monolayer on that interface, has been measured by us quantitatively. We applied the Near Total External Fluorescence technique (NTEF) for this experiment. The surfactant materials used in our study was stearic acid and the substrate solution was a 1×10^{-3} Mole solution of $Mn^{++}Cl_2$. The fluorescence signal from the Mn^{++} in the bulk as a function of the angle of incidence of the beam on the liquid surface is given in Fig. 1a. This data is consistent with having the Mn^{++} evenly spread in the solution. When a stearic acid monomer was spread on the surface and the experiment repeated (fig. 1b) a large fluorescence signal appeared around the critical angle. It indicates that the Mn ion is strongly adsorbed now to the surface. The solid line in both figures is a fit with a theoretical curve calculated using the coupled Fresnel equations with the appropriate optical parameters for both cases. The ratio of Mn ions segregated to the surface to the number of Stearate chains on the surface derived from this fit was 1.05 ± 0.2 .

Figure 1. Measured fluorescence intensity (circle) and the fit (solid line) of Mn(K-alpha) from the Mn-stearate monolayer on the substrate (b) and from the substrate alone (a).

This work was partially supported by the department of energy ,BES-Materials Sciences, under contract W-31-109-ENG-38.

FIRST SURFACE EXAFS FROM SURFACTANT MONOLAYER ON LIQUID

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Surface Extended X-ray Absorption Fine Structure (SEXAFS) has been applied by us for the first time to investigate the local order acquired by a monomolecular Mn-Stearate film spread on the surface of water solution. In the experiment, X-rays were incident on the sample at an angle smaller than the critical angle. Therefore only those Mn ions within a thin layer at the interface were excited and fluorescence from those ions was measured. SEXAFS in the condensed and the expanded phases of the Mn-Stearate monolayer was measured. The peak at around $1.5\text{\AA}$ (see Fig.1) was interpreted as the Mn-O distance. In the condensed phase, an additional peak (see Fig.1a) appears at a distance of about $4.1\text{\AA}$ after phase correction and this was interpreted as the Mn-Mn distance. This distance corresponds well with that measured previously in the Mn-stearate monolayer withdrawn to a solid substrate. The presence of the characteristic Mn-Mn distance in the condensed phase and the absence of this distance in the expanded phase reveals a different ordering of the monolayer in the condensed and the expanded phases.

Fig.1 The fourier transformed spectra of the fluorescence EXAFS from the condensed phase (a) and the expanded phase (b).

This work was partially supported by the department of energy ,BES-Materials Sciences, under contract W-31-109-ENG-38.

SCATTERING OF X-RAYS FROM SMOOTH SURFACE - THEORY VS. EXPERIMENT*

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The Optical Metrology Laboratory in the Instrumentation Division at BNL has been engaged in the development of metrology techniques to evaluate the surface finish quality of optical components to be used in NSLS beamlines. Our goal is to be able to predict the performance of x-ray optics under actual operating conditions based on our laboratory metrology techniques. To this end we performed a set of experiments on a super-smooth Au-coated SiC plane mirror to compare the measured scatter to predictions based on measurement of the power spectral density (PSD) of the surface roughness.

The basic angle-resolved scatter equation in the grazing incidence approximation is:²

$$(1) \quad \frac{1}{I_1} \left(\frac{dI}{d\theta} \right)_s = (1-g) \cdot R(\theta_1) \cdot \delta(\theta_s - \theta_1) + 16\pi^2 \left(\frac{\sin \theta_1}{\lambda} \right)^3 R(\theta_1) \cdot K \cdot S(f_x) \text{ where } S(f_x) \text{ is the PSD curve as}$$

measured by the WYKO profiler, and K is the theory-dependent materials-obliquity factor, which for the Rayleigh-Rice theory is:

$$(2) \quad K_{RR} = \left(\frac{\theta_s}{\theta_1} \right)^2 \left(\frac{R(\theta_s)}{R(\theta_1)} \right)^{\frac{1}{2}} \text{ where } R(\theta) \text{ is the Fresnel intensity reflectivity of the ideal surface.}$$

Measurements of the angular distribution of scattered light were made at beamline X19A with highly collimated monochromatic 8.9 keV photons. The incident beam was 100 μ m high; a 20 μ m slit was placed in front of an open air ionization detector and was scanned through the reflected and scattered beam in the vertical direction over a distance of several millimeters. Results for three angles of incidence are shown in Fig. 1 normalized to the direct beam intensity. These curves represent the left side of Eq. (1) with the finite angular size of the detector slit included. The peak specular intensities are used to adjust the values of n and k and the critical angle, according to the results of Bilderback,³ and are used in the calculation of R(θ). Figure 2 shows the calculation of the right side of Eq. (1) for each of the angles of incidence superimposed on the measured scatter curves. The Rayleigh-Rice theory correctly predicts the shape and magnitude of the scattering based on measurements of the surface roughness of the surface. It successfully explains the "Yoneda effect" asymmetry in the 8.593 mrad data and "anti-Yoneda effect" in the 3.864 mrad data.

Acknowledgments

The authors acknowledge the assistance and support of Dr. Peter Stefan in allowing us to perform the first experiment on X19A.

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*This research was supported by the U. S. Department of Energy: Contract No. DE-AC02-76CH00016.

STUDIES AND COMMISSIONING ON X-19A

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In this fiscal year, studies of beamline optical components were continued and initial beamline commissioning work begun. X-19A is an NSLS facility beamline, and negotiations for the formation of a special User Administration Group, to manage the beamline for general users, are underway.

Monochromator studies included testing of new first and second crystal holders. Modulation of the output x-ray beam through floor vibrations has been controlled in the new prototype second crystal holder. Use of Ga-In liquid metal in the first crystal holder now permits reduction of the clamping force required on the cooling blocks, and consequent reduction of strain in the crystal.

Commissioning of the beamline began with the testing of a VAX II-based data acquisition system developed by Mark Engbretson and Pedro Montano of X-18B. In addition to running the monochromator and accepting detector output, the system also controls 15 stepping motors which position various slits and a multi-axis table in the hutch. EXAFS analysis routines are also included in the package.

The monochromator was equipped with flat Si (220) crystals and covers an energy range of 3.5 to 12.5 keV. First EXAFS scans were made, but improvements in the main scan motor electronic drive and in the feedback stabilization systems are required. The re-focusing mirror was tested and produced a final focus of less than 1mm in diameter in the hutch.

Plans for the User Administration Group are being finalized. This group, composed of members of the EXAFS general user community, will manage the majority of the beamtime for general users, in exchange for a separate guaranteed fraction of the time. "Management" includes scheduling users and assisting general users in setting up experiments, becoming familiar with the computer system, logistics, etc.

A STUDY OF CREEP DAMAGE USING MICRORADIOGRAPHY

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We have shown, using the NSLS at Brookhaven National Lab., that cavitated grain boundary facets in iron and steel samples of about $100\mu\text{m}$ grain size and 1 to 2 mm thick can be easily observed using microradiography. The exposure times are approximately 10 minutes using Kodak High Resolution Plates, even though the sample (along with the film) is scanned through the x-ray beam in a periodic fashion through a range of several cms. to increase the exposed area. This is done because the beam size is smaller than the area we want to examine. We have also determined the minimum size defect that can be observed using this technique. The minimum dimension in the direction perpendicular to the beam is controlled by resolution. For beamline X-19C at the NSLS, a resolution limit of approximately $1\mu\text{m}$ in the direction perpendicular to the beam is obtained. In the direction parallel to the beam the minimum size defect observable is determined by contrast considerations. Assuming that a contrast of 10% can be seen on the film, a void of dimension $9\mu\text{m}$ parallel to the x-ray beam can be detected. Therefore, a single cavity $1\mu\text{m}$ in diameter cannot be seen by this technique, but ten such cavities aligned parallel to the beam or a microcrack $10\mu\text{m}$ long (parallel to the beam) can be detected. Figure 1 is an area from a radiograph of a notched iron sample which was tested at 700°C for 68 hours at a displacement rate of 2.11×10^{-5} mm/sec. The large white area is the macroscopic crack and the small white features are microcracks. It can be seen that the creep damage fans out from the crack tip.

The distribution of damage around creep cracks recorded on microradiographs has been analyzed using a microscope equipped with a digital analyzing system. Quantifying creep damage allows one to compare experimental results to theoretical predictions on the extent and distribution of creep damage around specific notch geometries. Figure 2 shows the results of the image analysis from an area of the crack tip region from the radiograph in fig. 1 (rotated by 90°). The numbers represent the area fraction of damage in units of 0.1%. The macroscopic crack is shown by the solid black region with greater than 10% damage. The concentration of damage can therefore be determined as a function of position, and contours of constant damage can be plotted.

Fig. 1 Radiograph of a notched iron sample tested at 700°C for 68 hours. The damage extends down to the bottom right corner of the radiograph, several mms. from the crack tip.

Fig. 2 Results from the image analysis of the crack tip region from the radiograph in fig. 1. The solid black region is the macroscopic crack.

In summary, we have developed a microradiographic technique using synchrotron radiation which can be used to quickly and reliably measure the amount and the distribution of creep damage in a sample. This technique is possible only because of the availability of a high intensity synchrotron source. The next step is to use this technique to test models of damage accumulation in metallic materials. Towards this end we have chosen a model material to study: high purity copper heavily doped with oxygen. Preliminary tests on the high temperature ductility of this material have been performed. A ductility minimum was observed at about 500°C , with a resultant reduction of area of about 3.1%. The fracture at 500°C was totally intergranular due to cavity coalescence. Further mechanical testing is currently underway at 500°C to determine the materials constants of deformation and fracture necessary for the finite element modeling of the damage accumulation process in this material.

Acknowledgements: This work was performed on the Synchrotron Topography Project beamline, X-19C, which is supported by the U.S. Department of Energy under grant DE-FG02-84ER45098. The image analysis was performed at the National Bureau of Standards with the assistance of Dr. R.J. Fields.

ANALYSIS OF X-RAY PENETRATION DEPTHS ON WHITE BEAM TOPOGRAPHS RECORDED IN GRAZING BRAGG-LAUE GEOMETRIES.

Michael Dudley, Jun Wu and Gong-Da Yao (SUNY SB - Dept. of Mat. Sci. & Eng.)

It is well known that the projective properties of white beam topographs recorded in transmission Laue geometries can be exploited to determine the spatial distribution of defects in a single crystal.^{1,2} In this experiment the projective properties of white beam topographs recorded in grazing Bragg-Laue geometries, from a silicon crystal with a well defined spatial distribution of defects, were used to enable direct determination of the depth of penetration of the X-ray beam into the crystal. The particular set of defects chosen for study consisted of a set of parallel 60 degree dislocations, of line direction $[101]$, and Burgers vector $1/2 [110]$. The projected lengths of the direct, or kinematical images of these dislocations depend on the relative orientations of crystal and detector and also on the length of defect sampled by the X-ray beam, which is determined by the penetration depth. Suitable analysis of the measured projected lengths of dislocation images enables the penetration depth to be determined. Results obtained can then be compared to penetration depths calculated from the kinematical and dynamical theories of diffraction, respectively. Generally, dynamical effects concede to kinematical effects as crystal quality deteriorates from perfect. Therefore, from the measured lengths of dislocation images one can also determine the nature of the local diffraction process.

Figure 1 shows a White beam reflection topograph taken from the $\{111\}$ crystal surface in the grazing Bragg-Laue geometry, with the detector normal to the incident white beam ($g = 022$, $\lambda = 0.4 \text{ \AA}$, $> 99\%$ fundamental). Note the very long projected dislocation lengths. Figure 2 shows a White beam reflection topograph taken from the same region of $\{111\}$ crystal surface in a slightly different grazing Bragg-Laue geometry, with the detector no longer normal to the incident beam ($g = 022$, $\lambda = 0.7 \text{ \AA}$, $> 99\%$ fundamental). Note the very short projected dislocation lengths. Analysis shows that the projected lengths of dislocation images measured from the topographs agree very closely with those predicted on the basis of kinematical diffraction theory. Results obtained convey two important points; (1) the assumption that in direct dislocation image formation, the regions immediately surrounding the dislocation line behave like miniature mosaic crystals, is validated. (2) the assumption that adoption of grazing Bragg-Laue geometries yields very narrow penetration depths (according to dynamical theory) is shown not to be general, but rather depends on the distribution of localized distortion fields in the crystal. In the regions immediately surrounding dislocation lines in a silicon single crystal, kinematical effects clearly dominate, and thereby determine penetration depths. It is to be expected that dynamical effects may still be valid in crystals where the local distortion in the crystal leads to effective misorientations, $\delta(\Delta\theta)$, which are smaller than the perfect crystal rocking curve width.

Fig. 1

Fig. 2

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Acknowledgments

Research work was supported by the Division of Materials Research, National Science Foundation, under grant number DMR-8506948. The topographic work was performed on the Synchrotron Topography project, beamline X-19C, which is supported by the U.S. Department of Energy under grant No. DE-FG02-84ER45098.

CHARACTERIZATION OF CRACK-TIP MICROSTRUCTURES VIA SYNCHROTRON FRACTOGRAPHY IN Mo AND Mo-Nb ALLOY CRYSTALS

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The nature of the plastic relaxation associated with the semi-brittle cleavage fracture of a series of pre-cracked Molybdenum-Niobium alloy single crystals has been investigated as a function of composition and temperature from 77°K to 298°K. Conventional optical microscopy and white beam Synchrotron X-Ray Fractography (SXRF) were used to examine the structure of a thin layer a few microns thick at the remnant of the precursor crack plastic zone.

The plastic work of fracture has been evaluated by measuring the lattice curvature associated with networks of dislocations beneath the cleavage surface. Using SXRF, lattice curvature is detected as asterism on photographic plates, and is associated with an excess density of edge dislocations of one sign. The results are in qualitative agreement with a previous determination of the fracture toughness of these specimens. Excess edge dislocation density of one sign has been shown to vary as a function of temperature and composition, in a way which is consistent with previous studies of total dislocation content in these materials. Unlike the etch pit analysis which can reveal the total dislocation content only, the tensor based analysis described here allows the activity on individual slip systems to be distinguished.

White beam fractography has been shown to be a novel method capable of revealing the crack tip defect structures left behind in the wake of crack propagation in single crystal specimens. It can be used on specimens for which no etchant for lattice dislocations is available. It reveals distortions of the single crystal lattice in all orders of diffraction, simultaneously in a single exposure, in a thin layer adjacent to the cleavage surface, and is nondestructive.

As such, the technique is a new method of fractographic characterization which has been applied to the technically interesting case of the Molybdenum-Niobium solid solution series. Although the analysis described here provides some insight regarding the crack-tip defect structure, its applicability is limited by diffraction effects and details of the mechanism of image contrast which detect only pure bend components of the total lattice curvature.

Acknowledgement

This work was performed on the Synchrotron Topography Project Beamline X-19C which is supported by the U. S. Department of Energy under Grant No. DE-FG02-84ER45098.

CRYSTALLINE IMPERFECTIONS AND THEIR ROLE IN THE REACTIVITY OF NaNO_3 AND NH_4ClO_4
SINGLE CRYSTALS STUDIED BY X-RAY DIFFRACTION TOPOGRAPHY

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Sections of solution-grown NaNO_3 and NH_4ClO_4 crystals were examined by both the Lang (sealed beam) and Synchrotron X-ray transmission topograph (XRT) methods and, both growth and post-growth line defects were characterized within the resolution limits of the techniques. The sections were sufficiently thick (up to 3 mm) to be fully representative of the material's bulk structure. It was found that Burgers vectors lie along the $[010]$ and $[001]$ directions in NH_4ClO_4 and the $\langle 111 \rangle$ and $\langle 20\bar{1} \rangle$ directions in NaNO_3 .

X-ray topographic observations of the changes in the microstructure of these crystals during x-ray radiolysis show that dislocations play no observable role in nucleating the chemical reaction for either material. In addition the dislocations were found to have no effect on the chemical processes induced in NaNO_3 by gamma-rays, UV light or thermal treatment. For both materials observations of resolvable line defects were limited to the early stages of the reaction as considerable strain was induced in the crystal lattice resulting from trapped gaseous product. However dislocation motion and/or generation due to either the stimuli or pressures exerted by the internally trapped gas was not observed.

Three types of chemical etch pits were formed on the cleavage surfaces of NaNO_3 crystals by glacial acetic acid. XRT showed that the large, (~ 80 - $100 \mu\text{m}$) asymmetrical, rhombic pits correlated well with dislocation outcrops of the type $(110) \langle 111 \rangle$. No correlation with existing dislocations was found for the remaining two types. The $(110) \langle 111 \rangle$ slip system was observed directly in room temperature in-situ tensile tests and was also found to explain; - (i) the XRT observed strain distribution around an indentation, (ii) the measured variation in Knoop hardness number as a function of position of the indenter's long diagonal, (iii) the observed etch pit alignments around indented and etched surfaces, and (iv) the observed microcracking that accompanied particular indenter orientations.

In NH_4ClO_4 Knoop hardness anisotropy measurements showed the $(102) [010]$ and $(001) [010]$ slip systems best described the data for the (001) face, while the $(100) [010]$ slip system best described the data for the (210) face. Both the $(001) [010]$ and $(100) [010]$ slip systems were observed by XRT.

Acknowledgement

This work was performed on the Synchrotron Topography Project Beamline X-19C which is supported by the U. S. Department of Energy under Grant No. DE-FG02-84ER45098.

STRESS STUDY OF NICKEL SILICIDE THIN FILM ON SILICON WAFER VIA SYNCHROTRON TOPOGRAPHY

YunJi Liu (SUSB SB) and A.H. King (SUSB (SB))

The stresses are of considerable importance in the use and application of silicide thin films in microcircuit technologies. Stresses can cause film rupture, loss of adhesion, and may introduce strain into the silicon substrates and cause dislocation generation or multiplication with its effects on the electric properties of some devices. In the present study, synchrotron topography was used to measure the stresses of nickel silicide thin films on Si wafers.

4" silicon wafers, both (100) and (111) oriented, were used as substrates. Nickel was coated on these silicon wafers by using resistance evaporation at pressures of 10 torr. Thicknesses ranging from 500Å to 2000Å were obtained. Nickel silicides were formed by rapid thermal processing at 600C for 5 seconds.

The study included the use of a Golovchenko double crystal monochromator to make high resolution strain studies. 1Å wavelength was used to obtain a glancing incidence beam on the sample with a large surface area imaged. A new sample holder was designed so there was no force on the samples examined. The Bragg contour mapping method was used to measure the radius of curvature of the wafers. From the measured radius of curvature the internal stress in the film can be calculated. The measurement was performed before and after the rapid thermal process, so the stress changes in the formation of silicide films could be studied. No large stress changes were observed in our experiment. Phases identification and structure studies of the thin film-silicon systems were performed by using TEM, STEM, EDAX techniques.

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Acknowledgement

This work was performed on the Synchrotron Topography Project Beamline X-19C which is supported by the U. S. Department of Energy under Grant No. DE-FG02-84ER45098.

AN EXPERIMENTAL AND THEORETICAL STUDY OF THE CRITICAL FACTORS CONTROLLING THE MECHANICAL PROPERTIES OF MOLYBDENUM AND OF THE INTERACTION OF INTERSTITIALS WITH BODY-CENTERED-CUBIC TRANSITION METALS

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The experimental part of this thesis presents a new high-sensitivity technique for the determination of the strain field in perfect-to-highly deformed crystals. A sensitivity of one part in 10^4 has been attained, and the spatial resolution has been pushed down to 25 microns. This technique has been implemented at the Brookhaven National Synchrotron Light Source (NSLS) for the study of the strain field in the proximity of a stress raiser in Mo single-crystals. Variations of lattice spacing as high as 300% and angular misalignments of 100% over 25 microns have been detected. Interesting features such as the change in sign in the variation of the lattice spacing of the diffracting planes above and below the tip of the notch have been revealed.

As for the theoretical part, the suitability of the recently introduced Finnis-Sinclair potentials has been investigated for the study of highly defective systems. Equilibrium (phonon dispersion curves, phase stability) and non equilibrium (pressure versus volume behavior) properties have been calculated and compared with experimental data. A simple modification has been introduced to the Finnis-Sinclair potentials to extend their applicability to highly deformed systems. The available experimental evidence pertaining to several transition metal/octahedral interstitial systems has been critically analyzed, in the attempt to understand the features of an interaction potential capable of describing the host/impurity system. Angular-dependent three-body potentials have been found necessary in order to account satisfactorily for the available experimental evidence. The displacement field out to very far neighbors of the impurity -at least ninth- has been found to show marked oscillatory behavior superimposed on generally expected decay.

Acknowledgement

This work was performed on the Synchrotron Topography Project Beamline X-19C which is supported by the U.S. Department of Energy under Grant No. DE-FG02-84ER45098.

TRANSGRANULAR FRACTURE IN ZINC BICRYSTALS AS PROBED BY MONOCHROMATIC AND WHITE BEAM SYNCHROTRON X-RAYS

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Crack propagation at 77°K and 298°K was studied for low cycle prefatigued zinc bicrystals. One grain was fixed so that the basal cleavage plane was always normal to the tensile axis while the orientation of the other grain varied. Cracks usually nucleated in the latter grain after extensive plastic deformation. synchrotron X-Ray Fractography (SXRF) and Monochromatic Bragg angle Strain Contour Mapping (SCM) was used to examine the strain field of the crack in relation to the bicrystal boundary plane. Lattice curvatures due to crack opening strains were accurately determined for several pure tilt boundaries. The behavior of twist boundaries and random boundaries was also characterized by x-ray and optical examinations.

The lattice curvatures were interpreted in terms of crack opening displacements. This data was then used to approximate the fracture toughness or penetration strength of the grain boundary. A boundary affected zone (BAZ), apparently a consequence of accommodation slip, was clearly discerned; the size of the BAZ was found to be strongly dependent on the test conditions. The penetration strength of the grain boundary was not strongly dependent on the size of the boundary affected zone; but earlier stages of crack nucleation and growth may be influenced by this deformed region due to the inhibition of basal slip.

Pure tilt boundaries were inexplicably found to be several times tougher than a single crystal. This high toughness was attributed to a grain boundary crack tip relaxation process.

Many interesting phenomena pertaining to nonbasal cleavage, incompatible bicrystals, and fatigue behavior were observed and documented so that a comprehensive understanding of the range of bicrystal orientations and fatigue properties could be approached.

Acknowledgement

This work was performed on the Synchrotron Topography Project Beamline X-19C which is supported by the U. S. Department of Energy under Grant No. DE-FG02-84ER45098.

AN 'IN-SITU' INVESTIGATION OF THE DEFORMATION BEHAVIOUR OF MOLYBDENUM CRYSTALS VIA SYNCHROTRON X-RAY TOPOGRAPHY

V. S. Wakharkar (SUNY SB) and J. C. Bilello (CSUF)

In-situ deformation experiments provide a good basis for investigating the time dependent evolution of the microstructural features that exist in the deforming specimen under load and that do not lend themselves to observation using conventional techniques. Synchrotron X-ray Topography is being used as an in-situ probe to study these changes in 'bulk' Mo crystals under controlled conditions. The experimental set-up consists of a computer controlled miniature tensile stage mounted on the white beam camera assembly. The detector arm carries the microchannel plate image intensifier tube along with a solid state CID television camera for real-time detection, display and recording of Synchrotron X-ray Topographs; while high resolution topographs (5 microns) can be taken on Kodak SR5 film. Tensile specimens for the deformation experiments were made from large Mo single crystals prepared by the secondary recrystallization technique. The main metallographic feature of these crystals is the presence of 'island grains' which are embedded localized regions misoriented by about 10-15 degrees with respect to the single crystal matrix and about 50-300 microns in diameter. Room temperature tensile tests were carried out on the specimens at a low strain rate of the order of 10^{-4} /sec. The experimental results have indicated the existence of localized plastic deformation below the yield point in these Mo crystals. Slip initiation at stress levels of about 0.3-0.7 of the macroscopic yield stress was observed in specimens which were continuously strained at a low strain rate. The presence of 'island grains' had a pronounced effect on the deformation characteristics of these crystals. It was observed that microcracks were initiated preferentially near the island grain - single crystal interface. Synchrotron X-ray Topography was used to follow the localized deformation processes which lead to the formation of microcracks at the interface.

1a

1b

Figure 1a and 1b show the changes occurring in the (111) reflection at increasing stress levels. Note the localized deformation near the island grains.

Acknowledgement

This work was performed on the Synchrotron Topography Project Beamline X-19C which is supported by the U. S. Department of Energy under Grant No. DE-FG02-84ER45098.

GALLIUM ARSENIDE TOPOGRAPHY AT BEAMLINE X-19C

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W.S. Corak (Westinghouse Advanced Tech.)

General

The defect structure of gallium arsenide has been examined using white beam transmission topography as part of a continuing program. The specimens examined were three inch diameter, single crystal substrates from various suppliers in the "as received" condition. Figure 1 shows an enlarged view of one topograph.

Fig. 1. Enlarged topograph of gallium arsenide.

Fig. 2. Montage of topographs.

The wealth of information recorded in the topograph is apparent. There are two basically distinct defect structures which appear with variations in all the gallium arsenide topographs we have examined. They become most obvious if one assembles a photographic montage of topographs from adjacent locations on the specimen, as shown in Fig. 2. First is a fairly isotropic cellular network or mosaic-like structure which seems ubiquitous throughout the specimens. Second are the more striking highly linear arrays which are localized to a few areas, and generally appear to run radially.

Results and Discussion

There are some complications in extracting all the information available from the topographs. First, the diffraction process is such that the images are formed in reciprocal space. Consequently, the reconstruction of defect structures from their apparent images as diffracted from various sets of lattice planes is not simple. This problem is currently being addressed as an image processing problem in the authors' laboratory. The second complication is that only a part of the three inch diameter specimen is illuminated by the incident beam (because of the inherent limitations on the beam dimensions available at the NSLS). As indicated above, this limitation has been circumvented by making montages of adjacent images. Future work will utilize a change in the experiment geometry to eliminate the need for photographic montages.

Acknowledgements

This effort was supported in part by Westinghouse Advanced Technology Division, which also supplied the experimental samples. The work was performed at Beamline X-19C of the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy under Grant NO. DE-FG-02-84ER45098.

INITIAL STAGE ORDERING KINETICS IN Cu_3Au

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The kinetics of a first-order ordering transition is expected to be described by an initial stage of either nucleation and growth or spinodal ordering¹, followed by a later stage of domain-size coarsening. Because of the time resolution obtainable, previous scattering studies² of ordering kinetics have been limited to the later stage. Recently we performed a time-resolved x-ray scattering study of the initial-stage ordering kinetics in Cu_3Au at the IBM/MIT beamline X-20C. In order to obtain the best possible time resolution, the x-ray flux on the sample was maximized by the installation into the beamline's monochromator of W/Si multilayers having a 1.1% energy bandpass³. At the 8.1 keV x-ray energy used, a flux of 10^{13} photons per second was obtained in a 1 mm^2 spot under typical NSLS operating conditions (100 mA, 2.5 GeV). The samples studied were cut from melt-spun polycrystalline Cu_3Au ribbon and were resistively heated *in situ* in a He atmosphere. The sample temperature was monitored using an optical pyrometer. The scattered x-ray intensity was measured in real time with a position-sensitive detector based on a linear photodiode array³. In the experimental geometry the detector accepted a line of scattering $0.9 \text{ \AA}^{-1}$ long in k-space, which allowed us to study the changes in the (100) or (110) superlattice peaks with millisecond time resolution as the sample ordered.

For a typical data set, a Cu_3Au ribbon was initially annealed *in situ* at $450\text{--}500^\circ\text{C}$, well above the first-order transition point ($T_R = 390^\circ\text{C}$). The sample was then rapidly quenched to a new temperature, T_Q , below or just above the ordering point and held at constant temperature ($\pm 1^\circ\text{C}$). The x-ray scattering, sample temperature, and sample resistance were measured in real time as the sample was quenched and began to order. The sample temperature could be changed by 100°C and stabilized in approximately 200 ms. This was sufficiently fast that very little ordering took place during the quench (see Fig. 1). After each run, the sample was re-annealed to restore the disordered state and then re-quenched, so that many data sets at various T_Q were obtained from each sample.

For $T_Q > T_R$, the data show that the diffuse scattering from short-range order fluctuations equilibrates relatively quickly (in 5 seconds or less depending on T_Q). At progressively lower values of T_Q , the intensity of the diffuse scattering and the equilibration time increase. This trend continues uninterrupted as T_Q passes through T_R . In addition to this process, a larger increase in intensity characteristic of nucleation and growth is observed on a much longer time scale (several minutes) for quenches to temperatures just below T_R . As T_Q is lowered further, the time scales for the two processes merge so that they are no longer distinct. These results show directly and quantitatively how homogeneous nucleation and growth changes to spinodal ordering with decreasing temperature. Detailed analysis of the data is now underway. The measured superlattice peaks can be fit using a 3-dimensional Hendricks-Teller-type model based on the two common types of antiphase domain boundaries⁴. Figure 2 shows typical fits of the theory function to our data for a quench to 362°C . The densities of the two types of domain walls can be determined from the fits and the average domain size as a function of time and temperature can be calculated. This information will be compared with theories of ordering kinetics.

Fig. 1. Sample temperature and scattered intensity at wavenumber $1.58 \text{ \AA}^{-1}$ as a function of time after a quench from 447°C to 362°C .

Fig. 2. Theoretical fits to the scattered intensity near (100) at five times after the quench shown in Fig. 1.

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*This work supported in part by the National Science and Engineering Research Council of Canada.

X-RAY REFLECTIVITY STUDIES OF THE SURFACES OF LIQUID CRYSTALS

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We have carried out x-ray reflectivity measurements from the free surface of mixtures of 4-cyano-4'-n-nonyloxybiphenol (9CB) and 4-cyano-4'-n-decyloxybiphenol (10CB) at X22B. If the phase diagram for mixtures of 8CB, 9CB and 10CB is plotted as though the concentration n , of nCB, is a continuous intensive variable, then for small concentrations of 10CB, there is a first order nematic to smectic-A phase transition. The pure 9CB is near a tricritical point and for all mixtures that would have a value of $n < 9$ the nematic to smectic-A transition is second order.¹ All previous measurements of nematic phases that undergo second order transitions to the smectic-A phase indicated that the surface induced smectic order penetrates into the bulk exponentially with a penetration length that is equal to the bulk correlation length $\xi_1(T)$. Our present measurements show that for a system in which the transition is first order, the surface induced order penetrates into the bulk from two to four times further than the bulk correlation length. This is analogous to wetting phenomena and we are in the process of analyzing that data.

Partially supported by the National Science Foundation through Grants DMR-86-14003, DMR-85-13523

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HIGH RESOLUTION X-RAY SCATTERING STUDY OF CHARGE DENSITY WAVE MODULATION IN CHROMIUM

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During the last several years magnetic x-ray scattering experiments have been performed on a growing number of magnetic materials, which now include both bulk and thin film ferromagnets and antiferromagnets (1-4). For long-period modulated magnetic structures the high resolution available from synchrotron radiation and the sensitivity of x-rays to modulations of the charge density have particularly motivated the use of synchrotron techniques. In recent x-ray studies of rare earth metals, for example, new lock-in behavior and additional peaks, arising from lattice modulations accompanying magnetic ordering, were discovered (2). The explanation of these effects in terms of competing exchange and magnetoelastic interactions has led to a new description of the magnetic structure of rare earths based on the concept of spin discommensurations or spin slips. In contrast to the rare earth metals the magnetic structure of chromium lacks a well localized moment and is described by an itinerant spin density wave (SDW). In addition to the magnetic scattering located at Q , x-ray and neutron scattering studies have established the existence of higher harmonics at $2Q$ and $3Q$. The scattering at $2Q$ is believed to arise from a charge density wave accompanying the spin density wave or to exchange striction.

We have performed a high resolution x-ray scattering study of the charge density wave modulation in chromium at the National Synchrotron Light Source on X22B, using 2 mrad unfocused radiation of wavelength 1.7Å. A single bounce Ge(111) monochromator was employed with a standard six-circle spectrometer and Ge(111) analyzing crystal, all diffracting within the horizontal plane. The crystal was an oriented $4 \times 4 \times 0.1$ (mm)³ square ((100) normal to large face) grown from the melt and strain annealed at 1700 C for two days. The wave vector at $2Q$ was found to vary continuously between 170K and 10K, consistent with the results of earlier neutron diffraction studies of the magnetic wave vector at Q .

Figure 1. Temperature dependence of the scattering at $2Q$. Open and closed circles distinguish different cycles of the temperature taken with different thermometers. The dashed line is a horizontal reference. The arrow indicates the spin-flip temperature near 122K.

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X-ray diffraction of $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_{4-y}$ reveals two macroscopically segregated tetragonal (K_2NiF_4 -type) phases of nearly identical lattice parameter ($\Delta a/a \approx \Delta c/c \approx 10^{-4}$). These peaks show additional broadening upon cooling, consistent with a spontaneous monoclinic distortion, with an onset temperature of $\approx 150\text{K}$. These data are inconsistent with the orthorhombic distortion reported by others for Sr-doped La_2CuO_4 . By carefully reducing the size of the highly collimated synchrotron x-ray beam we were able to isolate and study individual $\approx 70\mu\text{m}$ single crystals in the powder aggregate, using a novel high resolution Weissenberg camera that we have developed. These experiments confirm the interpretation of the powder data, and show that major and minor phases can coexist within a single macroscopic crystal. The brightness of a synchrotron x-ray source was essential for these high resolution powder and single crystal diffraction experiments. The observations of a minor phase in this sample, and also in a series of Sr-substituted compounds,¹ suggest phase separation within a nominally single-phase field as a motif in these oxides. The form and extent of this phase separation may depend both upon elastic anisotropy and on thermal and/or oxygen treatment.

Fig. 1. FWHM ($\Delta 2\theta$) of all of the measured Bragg peaks at 300 and 10K; the dashed curve is the measured instrumental width. Many peaks show an unusual broadening as the temperature is lowered.

Fig. 2. The widths of the (200) and (110) peaks vs. temperature, revealing a "transition region" at about 130-150K. Uncertainties in $\Delta 2\theta$ are about $\pm 0.005^\circ$.

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X-RAY REFLECTIVITY AND CRITICAL BULK SCATTERING FROM A MICELLAR LYOTROPIC LIQUID CRYSTAL

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We have performed x-ray reflectivity measurements from the surface of the lyotropic liquid crystal formed from Cesium-perfluoro-octanoate (CsPFO) and water as a function of temperature for the surface of both the isotropic and nematic phases using the free surface liquid spectrometer at X22B.¹ Preliminary analysis indicates that the surface induced smectic order in the nematic phase penetrates into the bulk exponentially with a characteristic length that is equal to the longitudinal correlation length for critical fluctuations in the bulk. This is identical to the behavior of surface induced order that we have previously observed for thermotropic nematic surfaces when the nematic to smectic-A transition is 2nd order. On the other hand the angular dependence of the peak in the specular reflectivity has a dispersive type of line shape, in contrast to the absorptive shape that is typically observed at the surface of all thermotropic nematic phases. This data is currently being analyzed.

As demonstrated with the thermotropic samples, the critical scattering from the bulk phase below the surface can be measured using the free surface liquid spectrometer. The advantage, however, is that the presence of a free surface often results in considerably improved alignment of the bulk phase. Measurements of the critical fluctuations in the bulk of CsPFO have a very different line shape than that of typical thermotropic nematic phases, suggesting that $\xi_{\parallel}$ may be larger than $\xi_{\perp}$. This is particularly interesting since thermotropic liquid crystals always have $\xi_{\parallel}$ longer than $\xi_{\perp}$. In view of the fact that the nematic unit in the micelles formed by CsPFO are believed to be oblate, or disk shaped, while the molecules that form thermotropic nematic phases are prolate, or rod shaped, the difference in the ratio of the correlations lengths appears to be directly related to the shape of the nematic unit. This data is currently being analyzed.

Partially supported by the National Science Foundation through Grants DMR-86-14003, DMR-85-13523 and by the Joint Services Electronics Program (U.S. Army, Navy, and Air Force) through Grant JSEP No. N00014-84-K-0465.

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SEARCH FOR CHARGE DENSITY WAVES IN A SINGLE CRYSTAL OF POTASSIUM BY SYNCHROTRON X-RAY DIFFRACTION*

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In the conventional description of a metal, the conduction electrons are uniformly distributed in a background of ion cores and, to a good first order approximation, behave independently. Because this nearly free electron model has not explained certain properties of even the simplest metals, such as K, Na, Rb, and Cs, an alternative model was suggested by A.W. Overhauser 25 years ago. One direct consequence of CDW phenomena is a periodic modulation of ion-core lattice to neutralize the CDW's which should produce a unique pattern of satellites around Bragg peaks in diffraction experiments. Despite several diffraction studies CDW satellites have not been found until recently Giebulowicz, Overhauser, and Werner¹ performed a key neutron diffraction experiment and reported the observation of CDW satellites in a single crystal of potassium. Since the discovery of CDW satellites have profound effect on the fundamental description of simple metals, we performed synchrotron x-ray diffraction study on single crystals of potassium to further explore satellites not accessible by the neutron study. The reported satellite intensity at A-D positions shown in Fig. 1 were 1.5×10^{-5} of (110) Bragg intensity and the other expected satellites were obscured by the nearby strong Bragg reflection in the neutron study. With high momentum-resolutions due to the extremely high collimation of synchrotron radiation, we were able to scan all the satellite positions (marked by letters) with a sensitivity of 10^{-7} (110) Bragg intensity. We have been unable to confirm the existence of any of the CDW satellites in spite of such high sensitivity. It is possible that the CDW satellites are much broader than the Bragg peaks in potassium and thus escape detection in our high resolution experiment although they would appear sharp with the poorer resolution of neutron experiments. We therefore performed additional experiments with somewhat reduced sensitivity but with resolution comparable to that of the neutron study. These experiments also failed to reveal CDW satellites. Our results² are summarized in Fig. 2, which shows the range of CDW satellite integrated intensity (~CDW strength) and width (~inverse CDW coherent length) which are compatible with our observations.

Fig. 1. (hko) plane around (110). Twelve CDW satellites positions with highest predicted intensities are marked by letters. All the CDW satellites (small circles) are located on the surface of a sphere (big circles) around (110). The satellites on a same large circle have the same L value as specified.

Fig. 2. Detectability diagram of our measurements. The area NEUTRON is the assumed confidence region of the neutron study. The unshaded region is rejected with the 99.5% significance test.

* Supported by Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016.

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X-RAY REFLECTIVITY FROM SOLID SURFACES

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We have continued our studies of the X-ray reflection from silicon surfaces using the Harvard MRL Rotation Anode X-ray Source (RAXS) and X22-B beam line at NSLS. We have investigated the structure of silicon surfaces coated with silanes of varying hydrocarbon length and terminations (straight chain hydrocarbons of the form $\text{SiO}_3-(\text{CH}_2)_n\text{-X}$). The silicon is bonded to the surface silicon oxide layer and cross linked to other silane molecules. For normal alkanes the termination group X is simply CH_3 however we have studied samples where X is $-\text{COOH}$ and CB_4 . The layers were formed as self assembling monolayers from solution.

From analysis of the ratio of the measured reflectivity to the ideal reflection from a sharp, flat surface the electron density normal to the surface can be determined. Destructive interference between X-ray's reflected from the hydrocarbon-air and the hydrocarbon-silicon oxide interface determine both the thickness and homogeneity of the coating. The thickness of the coating agrees with the values inferred from optical ellipsometric measurements to within 10% of the molecular length. In addition, non-harmonic interference minima were found at larger angles suggesting other subtle aspects of the surface structure.

We have found previously unreported x-ray damage of the monolayers and XPS analysis of the damaged has identified the change to be the oxidation of carbon atoms in the silane chain. This damage affects the specular reflection at large angles and was detected through a large reduction in the contact angle with water where the x-rays had illuminated the surface.

The structure of the silanes have been analyzed by taking the Fourier transform of the normalized reflectivity to directly obtain the autocorrelation of the derivative of the surface density profile normal to the surface. Although the previous analysis technique, in which the reflectivity was calculated from hypothetical models of the surface density profile, was able to explain the observations it was not possible to prove uniqueness of the density profile.

The basic results from both analysis techniques is that the width of the interfaces between the vacuum/hydrocarbon and hydrocarbon/silicon oxide layers are both approximately 3 Angstroms when the coatings are fully formed. Partially formed silane layers are shorter suggesting tilted molecules. In addition the width of the vacuum/hydrocarbon interface in partially formed layers is larger (i.e. 5 Angstroms) than the corresponding interface with the fully coated layer.

There is a SiO_2 layer on the surface of the bulk Si that is generally believed to be between 10A and 20A thick. We have found preliminary evidence of this layer but further experiments will be necessary to confirm this interpretation. We have also investigated the use of x-ray scattering to study the physical effects of chemical changes in the silane monolayers through changes in the termination.

Partially supported by the National Science Foundation through Grants DMR-86-14003*, and by the Joint Services Electronics Program (US Army, Navy, and Air Force) through Grant JSEP No. N00014-84-K-0465.**

X-RAY IMAGING FOR MICROTOMOGRAPHY AND MICRORADIOGRAPHY¹

Ronald C. Dobbyn (NBS), Masao Kuriyama (NBS), and Shozo Takagi (ADA)

Success in achieving one micrometer or better spatial resolution in two-dimensional x-ray imaging is dependent on three prime factors: (1) providing a sufficiently parallel incident beam (2) at sufficiently high flux levels and (3) providing two-dimensional imaging detection with sufficient spatial resolution and sensitivity. The highly-parallel, monochromatic, variable-area beam (5-30 keV) available at the X-23-A3 beamline and the use of two-dimensional diffraction image magnification^{1,2} before detection have been used to demonstrate a unique approach to achieving these goals.^{3,4,5}

Progress toward providing a high-resolution microtomography capability at the X-23-A facility was made during this reporting period. Two-dimensional imaging of biomaterials, ceramics and alloys was continued. Radiographic images, magnified up to 120 X (13.2 keV) before detection were obtained. At higher magnification levels evidence of polishing artifacts in the x-ray optics has become evident. However, one micrometer spatial resolution after image magnification, with existing image detector technology, has been achieved and flux levels have been sufficient for real-time video display. Scatter rejection, inherent in the x-ray image magnification process, is dramatic.

An AT/PC-based image processing computer and peripherals for use at the beamline have been received. This limited image analysis capability will provide the capacity for differential absorption microtomography, microradiography and depth-profiling in diffraction imaging as well as verification of successful data acquisition for complete tomosynthetic reconstruction on much larger computers. A complete implementation of this system awaits restoration of operations at the x-ray ring.

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¹Work supported by IMSE, NBS and USPHS Grant DE 05030

TOTAL REFLECTION EDXRF USING MONOCHROMATIC SYNCHROTRON RADIATION: APPLICATION TO SELENIUM IN BLOOD SERUM¹

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Several papers have recently appeared which describe the salient features of synchrotron x-radiation for the EDXRF analysis of metals at ng/g (ppb) levels. Because of the small source size and natural collimation of synchrotron radiation exiting the storage ring, x-rays can be directed with high precision at small glancing angles to the specimen and are particularly effective for use in the total reflection geometry. In addition, the high degree of polarization, high intensity, and continuous tunability of the beam energy are contributing factors for obtaining good analytical sensitivity.

The motivation for this work stems from the need for a blood serum reference material in which the selenium content, present at natural levels (e.g., 30-100 ppb), is known. Selenium in pure solutions and in NBS-SRM 1643b (Trace Elements in Water) was also measured for comparison. Minimum detection and quantitation limits (mdl) were calculated to characterize instrumental performance with the intent of developing a sensitive analytical method for the certification of such elements at ppb levels in future NBS SRMs.

The instrumentation at the NBS beamlines (port X-23A) was designed at NBS for diffraction imaging, spectroscopy, small angle scattering and energy dispersive experiments and has been described elsewhere.[1] The x-ray beam energy is tunable from 5 to 30 keV with a bandpass of 0.01% (at 8 keV), using a pair of asymmetrically-cut, flat silicon (111) crystals. For the total reflection geometry experiment the X-23-A3 micropositioning facilities were easily adapted to the scheme shown in Figure 1. An mdl of 8 ppb was determined for selenium in human blood serum and in proposed NBS-SRM 1598 bovine serum. The results show that this method is sufficiently sensitive for analysis of Se in blood serum. Se is present at about 30-100 ppb in human blood serum and about 40 ppb in NBS-SRM 1598. The lowest concentration of selenium measured was 9.7 ± 0.5 ppb in NBS-SRM 1643b-Trace Elements in Water where a mdl of 0.6 ppb Se was obtained. Spectra are shown in Figure 2. Mdls were also calculated to compare relative sensitivities of tube-excited secondary target conventional sources when illuminating a large sample area with NSLS excitation when probing a much smaller sample area.

Although this technique was examined in light of possible applications to non-destructive analysis, one should not lose sight of the fact that with appropriate sample dissolution, matrix separation and concentration of the analyte in small volumes, the sensitivity can be greatly increased and the analysis of samples containing trace elements at sub-ppb levels should be possible providing always, of course, that the blank is acceptable.

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Figure 1.

Figure 2.

¹Work sponsored by the Department of Commerce at the National Bureau of Standards

ANGLE-RESOLVED IMPERFECTION SCATTERING IN DIFFRACTION IMAGING¹

Ronald C. Dobbryn (NBS), Bruce Steiner (NBS), and Masao Kuriyama (NBS)

The quantitative analysis of the microstructure of materials revealed in diffraction images (topographs) requires a thorough analysis of the scattering of photons producing the images. The intensity distribution (contrast) observed in these complex images depends upon the glancing angle even at slight deviations from the Bragg condition, and arise from two basic phenomena, misorientation contrast and extinction contrast. Misorientation contrast is produced by dynamical diffraction from otherwise perfect crystal regions (mosaic blocks) which are separated by subgrain boundaries and are slightly misoriented with respect to one another or are misoriented in a continuous fashion as the result of homogeneous strain fields. Contrast occurs when beams diffracted from these regions separate or overlap. For a sufficiently parallel incident beam subtle contrast occurs when different blocks diffract from different parts of the rocking curve. In this case, there is no additional divergence introduced in the diffraction process ($\Delta k=0$); such intensity distributions can be explained adequately by perfect crystal diffraction theory. Extinction contrast is the result of scattering of the dynamically propagating photon field within the crystal by imperfections (e.g. dislocations, voids, stacking faults, localized non-homogeneous strains, etc.). Therefore, additional divergence is imparted to the beams that make up the image ($\Delta k \neq 0$). This divergence manifests itself in the blurring of these imperfection images when the detector is placed too far from the diffracting sample and also in the additional increase in the acceptance angle for diffraction from the sample (mistakenly called "larger rocking curve width" since rocking curve is an attribute of perfect crystal theory). Dynamical theories for a perfect crystal cannot describe this phenomenon. It is possible to describe this imperfection scattering analytically^{1,2}; the results of this analysis lead one to attempt a line-broadening analysis of the imperfection images. However, only recently have the means to carry out such experiments become available. Very bright x-ray sources of small emittance and high-quality x-ray optics are required to produce the very parallel incident beam and analyzer crystals needed for an unambiguous analysis.³

Preliminary experiments were conducted at the X-23-A3 beam line in February, 1987 for the purpose of determining flux levels and qualifying analyzer optics. The images shown below are of the (004) symmetric surface reflection from the central region of an In-doped GaAs wafer, viewed through an analyzer crystal set for (333) symmetric diffraction of 10 keV photons. The object of the experiment is to accept or reject, at will, the misorientation (perfect crystal) contribution to the image. When successfully rejected, one is left with only that contribution to the image from imperfection scattering. Image (a) is that of the complex diffraction image (misorientation contrast plus imperfection scattering); image (b) shows the imperfection scattering images only. A simple test for total rejection of the misorientation contrast can be made by checking for contrast reversal (black-to-white) as one rocks the specimen over its range of diffraction (acceptance angle) while viewing the image through the analyzer crystal. Contrast reversal will not be observed if the analyzer crystal is fully rejecting the mosaic contribution. This is easily observed in real time video at the X-23-A3 beamline.

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(a)

(b)

¹Work sponsored by the Department of Commerce at the National Bureau of Standards

DIFFRACTION IMAGES OF REPRESENTATIVE OPTOELECTRONIC MATERIALS¹

Masao Kuriyama (NBS), Bruce Steiner (NBS), and Ronald C. Dobbryn (NBS)

Orders of magnitude improvement in communication capacity and in the speed of the processing of information in recent years has resulted from major advances in the purity, crystal perfection, and yield of silica and silicon. Continuation of these advances in performance is promised by other materials such as gallium arsenide, especially in modulated structures. For these anticipated advances to be realized, improvement in crystal quality to approach that now achieved in silicon is an essential requirement. In addition, fundamental guidance on the materials structures producing specific properties will be of seminal importance. With the flexibility now promised by the growth of crystals under microgravity, progress in both areas can lead to early application of the results.

Diffraction imaging of high quality crystals will play a central role in addressing both sets of questions, that is both in uniformity and in the determination of superior structures. As an initial aspect of collaborative activity to achieve high quality crystals through their growth in space, we have surveyed the state of the art of crystal perfection of gallium arsenide, both doped and undoped; cadmium telluride; and mercuric iodide. This survey has been undertaken in order to determine the nature and extent of various defects, investigate their origins, and correlate these with their performance.

Each of three samples of undoped gallium arsenide observed displays complex sets of dislocations, interacting to form a cellular structure, shown in Figure 1. Linear subgrain boundaries appear and disappear in each of these samples, but not in the doped sample. The structure of an indium doped sample consists of a central faceted region, shown in Figure 2, surrounded by a peripheral set of circular striations and separated from it by a region reflecting turbulence in the solidification process. Linear arrays of dislocations record slip planes in the outermost circumference.

Four samples of cadmium telluride are all more highly strained than are the gallium arsenide samples. All crystals display rectilinear features, suggesting that these are closely related to the growth process. The large number of mercuric iodide samples all surveyed all contained separate grains, differing in orientation with respect to one another by several degrees around a common crystallographic axis. Rectilinear features in this material, however, closely resembled similar structures in cadmium telluride.

Figure 1. Enlarged portion of transmission (220) diffraction image through an approximately 700 micrometer thick undoped gallium arsenide wafer taken at 10 keV. Both individual dislocations and their interaction, seen as cellular boundaries at lower resolution, are observed.

Figure 2. Enlarged central portion of transmission (040) diffraction image of a 800 micrometer thick indium doped gallium arsenide wafer taken at 10 keV. The central, faceted region shown is surrounded by a peripheral region of growth striations.

¹Work performed as a member of the Center for the Development of Crystal Growth in Space, sponsored by the NASA and industrial members of the Center, including Grumman and Rockwell

AN X-RAY MONOCHROMATOR CRYSTAL WITH A BUILT-IN PHOTODIODE¹

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Alignment of a double crystal x-ray monochromator requires a method to determine when the second crystal satisfies the Bragg condition. In the past, an ionization chamber or photodiode situated in the exit beam has been used to measure the diffracted power from the second crystal. The detector unavoidably introduces absorption and scattering. This disadvantage would not be serious if the detector were only in the beam temporarily; however, it is desirable to keep it there permanently for rapid monitoring and correction of the alignment.

A new alignment method described in this report is to measure the power absorbed by the second crystal, using a photodiode fabricated directly on the diffracting surface of the crystal. The photodiode may cover the entire surface for maximum sensitivity. As the crystal is rotated through the Bragg condition, the x-ray penetration depth passes through a minimum due to extinction. Consequently, the absorption also passes through a minimum. If the pn junction depth is comparable to this minimum x-ray penetration depth, then the photocurrent should pass through a minimum at the Bragg condition. This method obviously avoids the disadvantage of the older method.

A photodiode has been fabricated on a silicon <111> wafer (see Fig. 1). The thickness of the wafer is 2 mm, and the diameter is 5 cm. The starting material is n-type, with a resistivity of 4 ohm-cm. A 2 x 2 cm² area is boron doped by thermal diffusion to yield a boron concentration of $1.8 \cdot 10^{19} \text{ cm}^{-3}$ at the surface, and a pn junction depth of .54 microns. Aluminum electrodes, .70 microns thick, are deposited along the perimeters of the p-type and n-type regions.

The performance of the photodiode has been measured at 8 keV. The incident beam was prepared by a non-dispersive double crystal monochromator, using <111> diffractions from silicon crystals. The diffraction from the first crystal was symmetric, while that from the second was asymmetric, with a magnification factor of eight. This arrangement provides a beam sufficiently parallel to study the rocking curve of the photodiode. Figure 2 shows the power absorbed and diffracted by the photodiode as a function of angular deviation from the Bragg condition. The "absorbed power" is actually just the photocurrent. The diffracted power was measured by another photodiode placed in the diffracted beam. The FWHM of both curves is about 10 arcseconds, in agreement with the rocking curve width of 7 arcseconds for perfect single crystal silicon. Thus, the built-in photodiode does not degrade the x-ray optical properties of the crystal. Finally, the photocurrent signal is clearly suitable for precise alignment of the crystal.

Fig. 1. Photodiode Cross Section

Fig. 2. Photodiode Performance

¹Work sponsored by the Department of Commerce at the National Bureau of Standards

DIFFRACTION IMAGING OF HIGH QUALITY BSO: IMPLICATIONS FOR CRYSTAL GROWTH¹

Bruce Steiner (NBS), Uri Laor (NBS), Masao Kuriyama (NBS), and Ronald C. Dobbryn (NBS)

Bismuth silicon oxide (BSO) is of interest in advanced approaches to parallel reversible optical signal recording and real time optical signal processing because of its exceptionally large photorefractive and electrooptic response. For ultimate success with such technology, both optimization of these properties and a high degree of material uniformity will be required.

Examination of diffraction images of several slices from a high quality boule of BSO has enabled us to identify four types of microstrain patterns, growth striations, and interface boundaries, and to associate each with distinct aspects of the crystal growth.² Analysis of these strains has led to a detailed understanding of the formation of this material. The model developed suggests ways to realize further improvement in the degree of crystal perfection.

Figure 1 shows a transmission diffraction image of one slice displaying each of the features observed: division into five principal regions common to all slices, a region of high strain observed in two of the three slices, striations in the four peripheral regions observed in all of the slices, and fringes in the central portion of all slices. Figure 2 shows an abstracted version of these regions for this crystal and for the other two.

The striations record growth of the peripheral regions in the {101} directions at 45° to the principal growth direction, while the fringes record growth of the central region on a surface oriented about 2° from the crystallographic [001] direction. The regions of high strain are associated with the sudden cessation in the growth of one of the facets, followed by a gradual resumption. The Moiré effect in the central portion of Figure 1 results from strains caused by growth layering at the two faces of the crystal. Rotation in the orientation of the central fringes during crystal growth is correlated with changes in the growth rates of the various facets and thus with the temperature distribution and flow in the melt. The asymmetric growth patterns are associated with these changes in flow and growth rates.

Fig. 1. Transmission (060) diffraction image of slice of BSO crystal taken at 13.4 keV. Various types of strain are visible, each associated with distinct aspects of the faceted growth of the boule and with the intersection of these strains with surfaces of the slice.

Fig. 2. Abstracted version of the diffraction image shown in Figure 1, in solid lines, and of similar images of two other crystals from the same boule, in dashed lines. From the changes in position from slice to slice, the faceted growth of the boule can be deciphered.

¹Work sponsored by the Department of Commerce at the National Bureau of Standards

²Bruce Steiner, Uri Laor, Masao Kuriyama, Gabrielle G. Long, Ronald C. Dobbryn, and Armand Tanguay, Jr., "Diffraction Imaging of High Quality Bismuth Silicon Oxide with Monochromatic Synchrotron Radiation: Implications for Crystal Growth," accepted J. Crystal Growth (1987)

SURFACE EXAFS STUDY OF SURFACE BaO LAYERS ON TUNGSTEN SURFACES

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Surface EXAFS (Extended X-ray Absorption Fine Structure) of near monolayer BaO films on polycrystalline W surfaces has been measured above Ba L3 edge (~ 5247 eV), with a total electron yield technique in a UHV system. Bond lengths and coordination numbers of the first two atom shells around the barium adatoms were analyzed using the ratio technique. We found that the first two strong features in the Fourier transform of the EXAFS spectra, shown in the figure below, were from ~ 3 oxygen atoms and ~ 6 barium atoms, while no feature was observed attributable to the tungsten substrate atoms. A substantial Ba-O bond length contraction was observed for the surface BaO species, which is about 2.3 Å, in contrast to the 2.76 Å bulk BaO value.

Escape Depth of Electron-Detection EXAFS

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The sensitivity vs. depth into the sample was measured for electron-detection EXAFS as described by Kordesch and Hoffman. Samples consisting of a 100 Å iron film covered by various amounts of aluminum were used to compare electron yield as a function of aluminum thickness. Measurements made at the iron K edge in vacuum ($\sim 10^{-5}$ torr) gave a yield of the order of one electron per photon absorbed in the iron layer (see table below). The depth dependence was exponential with a decay depth of 1500 Å. Identical measurements made after filling the detector with one atmosphere of He gas showed an increase in the raw signal of almost a factor of 100, independent of depth (third column in table). Using a value of 30 eV for the ion-pair production energy in helium, this implies an average electron energy of about 2500 eV.

Thickness Å	e ⁻ per Photon Absorbed (vacuum)	Ratio of He to Vacuum
140	.66	81
200	.56	85
500	.43	90
1100	.36	82
2200	.16	68
6100	-	-

STRUCTURAL STUDIES OF EPITAXIALLY GROWN POLYCRYSTALLINE DIAMOND

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The work described in this report was undertaken to examine the possibility of using standard diffraction techniques with both a conventional x-ray source and synchrotron radiation to determine the crystallinity of a thin synthetic diamond films. Diamond films were prepared at Crystallume using plasma-enhanced CVD techniques. The films were deposited on a polished (100)-face of a Si single crystal to thicknesses varying from 0.2 to 0.5 μm . As a preliminary test of the epitaxial diamond surface effects, several Vickers hardness tests were run. The uncoated Si surface gave a Vickers hardness number of 900. Similar tests were made of the diamond coating; Vickers hardnesses near the thinner and thicker regions gave values of 1450 and 1854, respectively. The hardness of Si is in agreement with accepted values, whereas those of the diamond are slightly below that of bulk diamond.

The sample was then mounted on a computer controlled diffractometer and illuminated with radiation from a Cu x-ray tube operated at 30 kV and 20 ma. A diffraction spectrum was obtained by step scanning from 40° to 80° 2θ at 0.0167° intervals and counting for 25 s. at each step. The resulting spectrum, which was collected over a period of 22 h, revealed the presence of the diamond (111) and (220) peaks, but the peak to background ratio was too poor to allow any further characterization.

The sample was then mounted on a second diffractometer, controlled with the same software, and illuminated with monochromatized radiation on X23-B. The same 2θ range was scanned in steps of 0.25° at a count duration of 1 s with the monochromator set at 1.5 $\text{\AA}$. This spectrum, which was collected in only 10 m, is shown below. From the recorded positions of the diamond (111) and (220) peaks a unit cell parameter of $3.562 \pm 0.005 \text{ \AA}$ was determined; this is in agreement with the accepted lattice parameter for diamond. Using a calibration standard and assuming zero residual strains in the sample, the Scherrer equation was used in conjunction with the measured breadths of the diamond peaks to estimate the mean crystallite dimension. A value of 110 $\text{\AA}$ was determined. These measurements indicate that quality information can be obtained from thin films of low Z materials in relatively short time periods using synchrotron radiation.

STRUCTURAL ANALYSIS OF PLASMA SPRAYED NiCrAlY COATINGS

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The superalloy NiCrAlY (17% Cr, 6% Al, 0.5% Y, bal Ni by weight) is commonly used in the aircraft industry as a high temperature oxidation resistant coating material. The purpose of this study was to use EXAFS to monitor structural changes in NiCrAlY coatings which were ion implanted with vanadium. The nickel, chromium and vanadium K-edges were studied. Two doses of vanadium (2×10^{16} and 2×10^{17} ions/cm²) were implanted at 85 keV. The vanadium was implanted to a depth of several hundred angstroms. Photoelectron EXAFS spectra were collected from 150 micron thick plasma sprayed coatings. The photoelectron escape depth is approximately 1000 Å, which was similar to the implantation depth.

A Fourier transform of the nickel edge EXAFS signal from an unimplanted NiCrAlY coating showed that the nickel matrix had an fcc crystal structure. The transform of the chromium edge data taken from the same coating showed that the chromium atoms also resided in the fcc lattice. Figure 1 gives the vanadium EXAFS transform from the low dose coating. Two coordination shells are clearly resolved. When compared to the nickel and chromium transforms, Fig. 1 indicates that the implanted vanadium had a near neighbor environment similar to nickel and chromium.

The ion implantation increased the disorder in the NiCrAlY coating. Figure 2 shows the vanadium edge transform of the high dose coating. As compared to Fig. 1, the magnitude of the first shell at 2 Å was considerably reduced. Also, note that the ratio of the amplitude of the second shell to the first shell is considerably smaller in the high dose coating than in the low dose coating. The nickel and chromium transforms from the low dose implanted coating showed less disorder than the high dose, but more than the unimplanted coating.

The coatings were oxidized for 10 minutes at 900 C in an 80% Ar-20% O₂ atmosphere and reexamined using EXAFS, TEM and energy dispersive x-ray analysis (EDX). TEM and EDX revealed the presence of NiO, NiAl₂O₄, and possibly NiCr₂O₄ and NiCrO₃. The EXAFS data showed that there were no significant changes in the chromium transforms as a function of vanadium dose, and only a small change in the nickel transforms. This result was surprising because it was expected that the vanadium would have a large effect on the oxidation behavior of the coating.

*This work was performed under contract number N00014-85-C-2628 from the Naval Research Laboratory.

Fig. 1) Vanadium edge transform of low dose NiCrAlY coating.

Fig. 2) Vanadium edge transform of high dose coating.

RELATIONSHIP OF THE CONCENTRATION-DEPENDENT Ti CENTER
TO THE LiNbO_3 ORDINARY OPTICAL INDEX

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Using x-ray absorption techniques, the Ti center in congruent LiNbO_3 is shown to be concentration-dependent. The change in the Ti center takes place within the concentration range used for integrated optics and involves a displacement in the xy plane of the LiNbO_3 crystal lattice perpendicular to the polar axis. Reports in the literature indicate that as the ordinary optical index increases with increasing Ti concentration, an abrupt decrease in slope occurs at approximately the same concentration at which our data shows the Ti center itself changes. Simple theory based on a linear-combination-of-atomic-orbitals (LCAO) model suggests that the change in slope of the ordinary index vs. Ti concentration can be accounted for by the observed xy displacement of the Ti.

The figure shows Ti $1s$ x-ray absorption data for two samples of Ti-diffused LiNbO_3 . The curve labeled "diffused (la)" corresponds to a sample with $5 \times 10^{20}/\text{cm}^3$ near-surface Ti concentration. The curve labeled "diffused (hi)" corresponds to a sample with $2 \times 10^{21}/\text{cm}^3$ near-surface Ti concentration.

EXAFS STUDIES ON PLASMA SPRAY QUENCHED MATERIALS

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It is well known that the high velocity deposition of plasma melted particles, yields highly disordered and metastable structures in many metal alloys and ceramics. A Ni-Cr-Mo based alloy with a composition tailored to form an amorphous phase during rapid solidification conditions, was plasma sprayed in air and low pressure. Plasma spraying under atmospheric conditions (APS) generally provides a high rate of quench, due to cold air cooling of substrate. In vacuum plasma spraying (VPS) (usually a low pressure of 20-60 mbar), however, due to absence of convective cooling, the substrate temperatures are in excess of 800 C.

Figure 1 shows the Fourier transform of EXAFS for the Ni-edge in the APS coating. These results have been compared to that of a fully crystalline Ni foil standard. It is observed, that the higher order shells in the transform are suppressed with respect to that of a crystalline material and in addition show significantly lower amplitudes. The results indicate absence of long range order in APS coating. Figure 2 shows the Fourier transform of the EXAFS for the Cr-edge in the coating. The data indicates partial oxidation of the Cr during plasma spraying.

The transform for the Ni-edge of VPS coating (Fig. 3) shows significantly increased ordering as indicated by the increase in amplitudes of the transform. The Cr-edge data (Fig. 4) shows that Cr is substitutional in the FCC Ni-lattice in the VPS coating.

This work was supported by National Science Foundation grant number MSM 8513038.

Fig.1 Ni-edge APS coating.

Fig.2 Cr-edge APS coating.

Fig.3 Ni-edge VPS coating.

Fig.4 Cr-edge VPS coating.

APPEARANCE POTENTIAL X-RAY FLUORESCENCE SPECTROSCOPY

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Appearance potential spectroscopy has been practiced for many years. In essence, it simply involves ramping the energy of the exciting quanta across excitation edges and observing the onset of a signal. Because of the relative simplicity with which the energy can be controlled, electrons have been the conventional quanta employed. The signals which have "appeared", characteristic of the atoms being studied, have been either Auger electrons or x-rays. With the availability of variable x-ray energy from synchrotron beam lines, it becomes possible to use x-ray excitation to observe the appearance of the x-ray fluorescence signal. This technique is simply a variant of fluorescence EXAFS, where the magnitude of the absorption edge jump is a quantitative measure of the number of atoms present. In fact, a single measurement can provide information about the elemental concentration (from APXRF) and local atomic structure (from fluorescence EXAFS). The degree of EXAFS data available depends to some considerable degree on the resolution provided by the beam line monochromator; high resolution is required in many cases. APXRF, on the other hand, benefits from the increased intensity from a low resolution monochromator; a single device is perhaps the more desirable. Some compromise is necessary when both types of information are required.

The figures illustrate the APXRF/fluorescence EXAFS spectrum of a $24 \mu\text{g}/\text{cm}^2$ film of Fe, measured on beam line X-23B, using two mirrors and a Si double crystal monochromator as the beam line optics.

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X-ray absorption experiments at the potassium K-edge were performed on a series of polymer-salt complexes of poly(ethylene oxide) and potassium iodide at different temperatures and with varying salt concentration. The purpose was to study the structure of the polymer-ion complex through the transition from the room temperature phase with low ion mobility to the higher mobility phase at elevated temperature ($\sim 100^\circ\text{C}$). The potassium ion is complexed by the lone-pair electrons of the oxygen atoms of the ether moiety $(\text{CH}_2\text{CH}_2\text{O})_n$, as in an oxygen cage. The near edge structure of the potassium x-ray absorption spectra was compared with those of standards consisting of organic salt complexes where the potassium ion is complexed by 1, 2, and 6 oxygen atoms. As can be seen from Figs. 1 and 2, the change in the near edge structure with increasing temperature follows the same pattern as decreasing the number of oxygen atoms complexing the potassium ion. This indicates that, at elevated temperature, the increased mobility of the potassium ion is correlated with a decreasing number of complexing oxygen atoms, i.e. the potassium ion is less tightly bound to the polymer backbone. This interpretation is also supported by a more detailed analysis of the EXAFS region of the spectra as well as independent thermodynamic experiments.

Fig. 1. X-ray absorption spectra of a series of organic potassium salts with 1, 2 and 6 oxygen atoms complexing the potassium ion. The spectra were taken at room temperature.

Fig. 2. X-ray absorption spectra of poly(ethylene oxide)-KI salt complexes as a function of temperature. The salt concentration corresponds to four oxygen atoms of the polymer backbone for each potassium ion.

NOTE: This research was supported by the Division of Materials Science, U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

X-24A INSTRUMENTATION: PERFORMANCE OF A HIGH ENERGY RESOLUTION, TENDER X-RAY SYNCHROTRON RADIATION BEAMLINE

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Design Goals

Beamline X24-A is designed for optimal performance in the tender x-ray (i.e., firmer than soft x-ray) spectral region from 800 eV - 5000 eV. This choice of energy range places a number of constraints on the beamline design, requiring a crystal monochromator and at the same time a windowless environment. Nevertheless, there are compelling scientific reasons for our desire to work in this range [1,2]. In addition to tunability over the selected energy range, a primary goal is to obtain the highest possible energy resolution in the primary beam as discussed below. Finally, it is important to focus as much flux as possible from the bending magnet source at X24-A.

Design Features

A toroidal mirror was located downstream from the monochromator to enable full-aperture focussing without loss of energy resolution. Another mirror, which is effectively cylindrical in shape, was placed upstream of the monochromator to improve collimation of radiation incident on the monochromator crystals. The entire beamline was designed to rotate about the axis of upstream mirror to permit filtering of radiation prior to the monochromator. This feature is particularly important in allowing the use of multilayer coatings on the upstream mirror [2].

Resolution Considerations

The oft cited rule of thumb for synchrotron radiation beamlines is that the energy resolution need be no better than the core-level lifetime broadening for a given energy range. We have achieved energy resolution significantly better than the core-level lifetimes allow. This has permitted studies of processes that are not broadened by lifetimes, such as resonant scattering and back reflection x-ray standing wave effects [2].

Optimal resolution can be achieved by an appropriate choice of monochromator crystals for the selected energy range of a given experiment [1]. It is also possible to sacrifice energy resolution in exchange for higher flux by crystal selection. The design of the monochromator mechanism [3] permits additional gains in energy resolution or flux through the use of asymmetric crystals, or additional (i.e., >2) Bragg reflections.

Performance

To date the performance of only Si(111) crystals has been completely characterized. Measured energy resolution agrees with predictions but flux was initially <20% of prediction [1]. Subsequently, we have learned that a factor of 4 was lost due to problems with the NSLS apertures and orbit. Additional flux loss was due to excessive roughness of the toroidal mirror which has recently been repolished.

Initial studies of the performance of InSb monochromator crystals were thwarted when a shift in the storage ring orbit caused the white x-ray beam to miss our filtering multilayer and melt the first monochromator crystal. A direct beam block will be installed between the filtering mirror and the monochromator before testing of exotic monochromator crystals resumes.

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X24A INSTRUMENTATION: PERFORMANCE OF A MULTILAYER MIRROR AS A PRE-FILTER FOR A SYNCHROTRON X-RADIATION BEAMLINE.

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Multilayer-coated mirrors, rather than conventional total-reflection mirrors, have been proposed as a means to reduce power incident on the first optical element of high resolution monochromators. This work represents the first step toward implementing this concept in a synchrotron radiation beam line. We have designed, fabricated, installed and characterized a multilayer coated pre-mirror specifically for the 800-4000 eV range for the X24-A bending magnet beamline. The ultimate goal of this pre-mirror is to enable use of radiation sensitive crystals [1] in the 800-2000 eV range.

Many factors affecting the choice of the constituent multilayer materials and operating energy and angular ranges were considered in the design stages. We were lead to the relatively low-Z combination of amorphous SiC and V in a relatively large period structure for this application [2]. Figure 1 shows the calculated reflectivity of the SiC/V multilayer which was chosen to coat the pre-mirror compared to that calculated for the Ni-coated mirror which it replaced. The area above the multilayer reflectivity and below the Ni mirror reflectivity represents the additional power filtered out by the multilayer compared to the grazing incidence mirror. In this case the multilayer decreases the reflected power by a factor of 4.

Fig. 1. Comparison of calculated reflectivity of the multilayer and Ni-coated mirror.

Fig. 2. Measured pre-mirror reflectivity compared to the calculated reflectivity of the multilayer.

The multilayer pre-mirror was installed immediately prior to the 1987 shutdown. Characterization of the reflectivity as a function of energy at fixed angle was more easily accomplished than reflectivity as a function of angle at fixed energy. Figure 2 shows reflectivity data in a higher energy range than that intended for pre-mirror operation. Superimposed on Fig. 2 is the calculated reflectivity for the second order multilayer Bragg peak. The measured reflectivity has not been corrected for background or for varying detector efficiency with energy and is plotted on an arbitrary vertical scale. Since the second order peak is significantly narrower than the first order peak, this comparison strongly suggests that the multilayer on the pre-mirror was quite uniform, as the measured Bragg peak is not substantially broader than the calculated peak. Heating of the multilayer in the synchrotron beam was not observed to cause any degradation with ring currents in excess of 100 mA.

These results demonstrate the feasibility of utilizing multilayer pre-mirrors as power filters in synchrotron radiation beamlines. Calculations show that multilayers can reduce the power incident on a high resolution monochromator by as much as an order of magnitude compared to conventional total reflection mirrors. These preliminary results encourage further development of this multilayer power filter concept to ascertain whether this device will permit the use of more radiation sensitive crystals in the monochromator.

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This work was supported by the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

X-24A INSTRUMENTATION: PERFORMANCE OF A TUNABLE SECONDARY X-RAY SPECTROMETER

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Introduction

An efficient high energy resolution secondary x-ray spectrometer is critical to studies of x-ray excited x-ray emission spectroscopy. Even with the highest available incident flux of x-rays the signal count rate can become unacceptably low when dispersed by an analyzing crystal. This can especially be a problem in studies of gas targets, or at low energies where fluorescent yields are low.

Design of Spectrometer

A Rowland circle geometry with a curved (Johann) analyzing crystal was chosen to increase efficiency while maintaining good (i.e., <1 eV) energy resolution. A position sensitive proportional detector was used so that counts at different points of the Rowland circle corresponding to different wavelengths can be recorded in parallel. The source is positioned inside of the focus so that the source will subtend rays from a range of points on the Rowland circle.

By defocussing the source it is possible to collect data in parallel within a spectral window 15 eV to 50 eV wide. In most cases this is sufficient to record parent lines with all associated satellites or to observe the dispersion of resonant elastic or inelastic scattering.

The instrument can be tuned over a Bragg angle range from 30° to 60° . Since tuning is not required for data collection, this feature is primarily used to optimize the spectral window for the selected element and spectral feature(s) to be studied. Tuning is effected by a θ - 2θ UHV compatible parallelogram linkage [1]. During tuning the cord of the Rowland circle between the crystal and detector is constant. This serves both to simplify the scanning mechanism and to minimize the change in energy resolution for a given detector position resolution. Maintaining a constant cord length for changing angle requires an adjustable Rowland circle diameter and hence a variable crystal radius. This is accomplished by a novel crystal bender [2].

Efficiency

The expected efficiency for the spectrometer is on the order of one part per million. The high incident x-ray flux at X-24A compensates for this low efficiency to permit the observation of weak processes, such as sub-threshold elastic and inelastic x-ray scattering from gases with good resolution.

Resolution Performance

The spectrometer was designed with the assumption that the position sensitive detector resolution would be $120\ \mu\text{m}$ or better. To date the best resolution for our NBS built "Backgammon" detectors [3] was $200\ \mu\text{m}$ measured on a test stand with 8 keV x-rays. On-line at the NSLS the best measured resolution at 3 keV was $400\ \mu\text{m}$. This spacial resolution limits the energy resolution of the spectrometer at all but the lowest energies. Performance at the low energies, where the analyzing crystal becomes highly dispersing, is excellent. Near 2310 eV, resolution better than 0.7 eV has been obtained.

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This research has been funded in its entirety by the National Bureau of Standards.

X-24A Instrumentation: X-Ray Mirror Characterization for X-24A

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The NBS beamline X-24A was one of the first beamlines designed with two glancing incidence x-ray mirrors, and was the first such beamline to operate at a high brightness x-ray source. As such studies of the performance of the mirrors is critical in determining the advantages of such a design.

Pre-Monochromator Mirror

The first mirror is positioned upstream of the two-crystal monochromator and serves two functions. First it suppresses the high energy photon flux which reduces the power load on the first monochromator crystal and reduces problems with harmonics. Secondly, it is curved to improve upon the natural vertical collimation of the synchrotron radiation. This improved collimation is possible when the source size is sufficiently small.

For the initial 18 months of operations an electroless nickel coated, aluminum substrate mirror was used. The reflecting surface had a concave, spherical curvature with a radius of 1.1 km. Although provision was made for water cooling of this mirror, it was not used due to vibration problems with the NSLS water lines. Mirror temperatures as high as 100°C were observed, but no irreversible distortions of this mirror due to prolonged exposure to high power radiation were detected.

Tests of the effect of the mirror curvature on monochromator energy resolution have been performed. With low (i.e. <50 mA) storage ring current a 0.7 mm vertical aperture slit was positioned upstream of the mirror. Measurements of the narrow sub-threshold Ar absorption resonance were made for a variety of slit positions covering the full effective aperture of the mirror. The apparent energy of the resonance changed by ≤ 0.1 eV which implies the effective figure error of the mirror is ≤ 12 μ rad. However, at higher ring currents with larger aperture slits, noticeable degradation of monochromator resolution was observed. This degradation is believed to be due to temporary thermal distortions in the premirror caused by local beam heating of the mirror. A copper substrate mirror has been prepared and vibration-free water cooling is being considered to improve high power performance when the x-ray ring resumes operation.

The surface roughness of the mirror and its effects on the x-ray beam have also been measured. Surface roughness tends to reduce specular reflectivity and increase scattered intensity which appears in the tails of the reflected beam profile. We have measured the monochromatic beam profile at a number of photon energies and a number of incident angles and have observed only minor scattered intensity. This is consistent with profilometer measurements [1] of the surface which indicate a roughness of 2.5 nm.

Focussing Mirror

A second mirror is positioned downstream of the monochromator to collect the maximal horizontal divergence from the bending magnet source without degrading the monochromator energy resolution. The mirror is a torroid formed by bending [2] a cylindrically ground, fused quartz mirror with an evaporated nickel coating. Although beam profile measurements were not made for reflections from this mirror, noticeable scatter was apparent during observations made with a phosphor screen. Profilometer measurements indicated a surface roughness of 7 to 10 nm. This mirror has been repolished to <1.5 nm roughness and is awaiting resumed operations.

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This research has been funded in its entirety by the National Bureau of Standards.

X-24A NEW EXPERIMENTAL TECHNIQUES: ENERGY SELECTIVE EXCITATION OF X-RAY EMISSION SPECTROSCOPY

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Introduction

X-Ray spectroscopy is one of the oldest experimental techniques for measuring the electronic structure of matter. Traditionally, x-ray absorption spectroscopy has been used for studying unoccupied states and high energy resolution x-ray emission spectroscopy has been used to study the occupied states. Activity in these areas has declined over the past few decades partially due to the availability of other techniques, such as photoelectron spectroscopy, and partially due to a number of fundamental problems with the x-ray spectroscopic techniques [1]. The availability of high fluxes of highly monochromatic, tunable x-rays from synchrotron radiation sources combined with efficient, high energy resolution x-ray emission spectrometers opens a number of possibilities for circumventing the debilitating difficulties. The past year at beamline X24-A we have made great progress both in demonstrating how "well known problems" can be overcome and in opening new areas of study for x-ray spectroscopy.

Multi-Vacancy Effects

When x-ray fluorescence is stimulated by high energy excitation (either charged particles or photons) the emitted spectra include components associated with the presence of multiple vacancies in the fluorescing atom. These multivacancy components can obscure single vacancy features of interest, and impede the interpretation of the emission spectrum. It has been shown [2] that the multivacancy components of fluorescent spectra can be selectively suppressed or even extinguished by tuning the energy of the excitation x-rays to near the single vacancy threshold. In the past year we have applied this effect for the first time to the study of molecules and solids.

The production of multiple vacancies is in itself an interesting subject of study. Measurements of multi-electron transitions potentially can yield information about electron correlation. Also the creation of multivacancy states is fundamentally linked to the detailed understanding of Auger electron spectroscopy. We have made extensive studies of multivacancy states in a closed shell atom (argon) and have initiated studies of such effects in several molecules and one solid (KCl).

Lifetime Broadening

X-Ray fluorescence requires the production of an inner shell vacancy. Normally, the width of the fluorescent spectral components is determined by the lifetime broadening due to the short inner shell lifetime. However, when highly monochromatic x-rays are used to excite fluorescence, study of the final (post emission) state structure is limited only by the instrumental resolution. This avoidance of lifetime broadening is particularly evident in our studies of resonant fluorescence from atoms, molecules and solids.

New Effects

In addition to solving the long-standing problems above, energy selective excitation opens new possibilities. For example the excitation energy can be tuned such that an inner shell electron is promoted to a selected unfilled orbital. This excited electron can differentially screen the subsequent decay of the core hole from electrons in the various outer levels and shift the fluorescent energy accordingly. Studies of such differential screening shifts can provide information about the spacial configuration of the various orbitals involved. Related information can be obtained from observations of the polarization of the fluorescence components under these conditions.

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This research has been funded in its entirety by the National Bureau of Standards.

X-24A NEW EXPERIMENTAL TECHNIQUES: POLARIZATION ANALYSIS OF X-RAY EMISSION SPECTRA

P L. Cowan (NBS), R.D. Deslattes (NBS), T. Jach (NBS), R.E. LaVilla (NBS), D.W. Lindle (NBS), and B.A. Karlin (NSLS).

The x-ray emission spectrometer used at X-24A can also be used for polarization analysis of emitted x-rays. Maximum polarization sensitivity occurs when the Bragg angle of the analyzed radiation equals 45° , but significant polarization sensitivity can be obtained over a range of energies (see Fig. 1). The polarization of the emitted x-rays can be influenced by a number of factors including: orientation of incident beam wave vector, orientation of incident beam polarization vector, and orientation of the sample.

Figure 1 The ratio of Bragg reflectivity from a Si(111) diffraction for π and σ polarized radiation vs. energy.

Wave Vector

To first approximation, the intensity of elastic scattered x-rays with polarization parallel to the incident wavevector should vanish. On resonance, however, this intensity can become measurable. This effect is termed resonant depolarization of elastic scattering. This effect could provide an additional method for studies of resonant structure, particularly if studied in combination with other influences on polarization. We have studied resonant depolarization of elastic x-ray scattering from Ar [1] and molecular gases.

Sample Orientation

Pronounced polarization-dependent effects have been reported for x-ray absorption which are a function of orientation for solid samples [2]. Similar effects have been predicted for x-ray emission [3]. Although we have not studied polarization of emission from solid samples we have seen polarization effects from gases which strongly imply the importance of sample orientation.

Incident Polarization

Synchrotron radiation tends to be polarized parallel to the plane of the electron orbit. This natural polarization can be further enhanced when the radiation is filtered by a two-crystal monochromator. When tuned to a sub-threshold resonance of a molecular gas, the polarized incident beam may excite only those molecules with particular orientations. The orientations which become excited depend upon the driven resonance and the symmetry of the unoccupied orbitals involved in the resonance. The resultant aligned, excited atoms can then emit x-rays which will be polarized depending on the molecular orientation and the electron orbitals involved in the x-ray emission. We have studied this effect for a number of molecular gases [1].

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This research has been funded in its entirety by the National Bureau of Standards.

X-24A NEW EXPERIMENTAL TECHNIQUES: DEVELOPMENTS IN BACK-REFLECTION X-RAY STANDING WAVE ANALYSIS

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The X-Ray Standing Wave technique, which is based upon microscopic interference between incident and diffracted x-rays, has become a useful tool for precise determination of atomic structure. However, the application of the technique has largely been limited to those few materials which are readily available as highly perfect crystals. This is due to the fact that even a slight strain or mosaic spread in the sample crystal is enough to disrupt the x-ray interference.

It has long been realized that the crystal perfection constraint could be relaxed if the x-ray standing wave technique were established in a back-reflection (i.e. a Bragg angle of 90°) configuration. In this case the natural rocking curve width of Bragg diffraction can approach tens of milliradians. However, a number of technical obstacles had to be overcome to take advantage of this fact. First, the back-reflection condition constrains the energy of the x-rays at which diffraction occurs. For most crystals this energy lies roughly between 2 keV to 4 keV for the low index planes. Synchrotron radiation sources allow one to choose an appropriate energy and still retain high photon flux, but few beamlines are capable of working in this energy range. Secondly, although the angular width of the diffraction condition gets big in back-reflection, the energy width is relatively unchanged at about 1 eV or less. Thus relatively high energy resolution must be achieved in the incident beam monochromator.

Demonstration experiments of the back-reflection x-ray standing wave effect have been independently reported from other synchrotron radiation facilities [1, 2]. We have employed a number of features not included in the other work. We were able to directly detect the diffracted beam by using a transparent photodiode. We detected characteristic x-ray fluorescence in addition to Auger electrons. Also, we were able to observe the total or partial electron yield from the sample. We also had at our disposal the high x-ray flux and high energy resolution available from beamline, X-24A. Finally, we were able to observe more than one diffraction from a single sample by simply tuning the monochromator to a new energy and rotating the sample crystal.

The importance of high energy resolution is illustrated below. Shown is the Cl x-ray fluorescence vs. incident photon energy during diffraction from Cu(200) for Cl adsorbed on a Cu(100) surface. Note that the fluorescence varies from maximum to minimum with a change of $<1\text{eV}$ in the monochromator energy.

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X-24A ATOMIC PHYSICS: STUDIES OF ARGON K-EDGE ABSORPTION

S. Brennan, J. Cooper, P.L. Cowan, R.D. Deslattes, T. Jach, R.E. LaVilla (NBS), and B.A. Karlin (NSLS)

Although argon is a mono-atomic gas, its K-edge absorption spectrum exhibits a wealth of detailed structure [1]. With the improved energy resolution available from beamline X-24A, we have extensively remeasured this structure. Furthermore, recent calculations by Cooper [2] are being compared with our improved measurements.

Features of interest in the argon absorption spectrum can be divided into three classifications: the sub-threshold Rydberg series, the single vacancy threshold region, and the multivacancy resonance and threshold region. Modeling of the Rydberg series can determine parameters used for calculations of inelastic scattering [3]. The steep fall off of the near threshold single vacancy cross section has not previously been matched by theory [1]. However, recent calculations by Cooper [2] agree with preliminary analysis of our data to within experimental error. Additional calculations by Cooper [2] suggest a revision of the previous assignment [1] for the largest multivacancy absorption resonance.

Figure 1. Measurement of multivacancy absorption structure for argon.

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This research has been funded in its entirety by the National Bureau of Standards.

P.L. Cowan, S. Brennan, T. Jach, R.E. LaVilla (NBS), and B.A. Karlin (NSLS)

We have conducted a detailed study of inelastic x-ray scattering from an atomic gas (argon) for incident photon energies near the $1s$ threshold. Studies of the inelastic scattering process from a closed shell atom provide an ideal test for of the current understanding of this phenomenon. This understanding is basic to our studies of molecular and solid samples [1] which have indicated important potential applications of inelastic x-ray scattering involving sub-threshold resonances.

Theoretical analysis by Tulkki [2] has provided a simple model for understanding resonant inelastic scattering. This model describes the relationship between sub-threshold phenomena such as resonant Raman x-ray scattering to super-threshold emission in the form of x-ray fluorescence. We have compared this model to our data and have found that quantitative agreement is achieved with no adjustable parameters.

Particularly striking is the sub-threshold narrowing of emission features which occurs both in the theory and experiment (see Fig. 1). Comparison shows that resonant emission

Figure 1. Emission spectra in the Ar K region stimulated by resonant (solid) and super-threshold (dashed) incident x-rays.

is obviously narrower than fluorescence excited above threshold, but perhaps more significant is the shape change of the emitted peaks. Non-linear least squares fits of the data indicate that while the super-threshold excited emission peaks exhibit Lorentzian tails characteristic of $1s$ lifetime broadening, the resonant peaks are fit by a Gaussian shape. The Gaussian peak shape is characteristic of the measured instrumental response of the secondary spectrometer, indicating that additional sub-threshold narrowing may be observable with improved spectrometer performance. This opens the possibility of high resolution studies of electronic structure which circumvent inner-shell lifetime broadening limitations.

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This research has been funded in its entirety by the National Bureau of Standards.

X-24A ATOMIC PHYSICS: THE ORIGIN OF THE ARGON $K\beta$ SATELLITE IN THE $K\beta$ EMISSION SPECTRUM

R.E. LaVilla, S. Brennan, P.L. Cowan, T. Jach (NBS), and B. Karlin (NSLS)

The main features [1] of the argon $K\beta$ emission spectrum consists of the main line $\beta_{1,3}$ and its satellite complexes β^V and β'' positioned 3 eV and 7 eV respectively on the high energy side of the parent $\beta_{1,3}$ line. We had demonstrated earlier in a double differential experiment [2] that the $\beta_{1,3}$ line is due to the single vacancy transition $3p \rightarrow 1s$ and that the satellites are multivacancy transitions. In particular the β^V satellite was shown to be primarily transitions based on the $1s3p$ configuration with contributions from double and single ions and excited neutrals. The satellite β'' has been suggested to originate from $1s3s$ double vacancy [2] or $1s3p^2$ triple vacancy [3] initial states. An accurate measure of the energy threshold of the β'' emission feature should help clarify the origin of this satellite feature.

The argon $K\beta$ spectrum in fluorescence was obtained with a secondary spectrometer as a function of incident excitation by x-rays from the primary monochromator on beamline X24-A. The energy of the incident exciting x-rays was monitored by repeated measurement of the argon K absorption edge profile. The satellite β'' feature becomes evident in the $K\beta$ emission spectrum when the incident excitation is 46 eV above the argon K threshold (3206.0 eV) in good agreement with our previous determination.

The $1s3snsnp$ channel opens at about 32 eV above the $1s$ threshold with the double ionization threshold at about 48 eV. The neutral and single ionized $1s3s$ Rydberg states can decay by Coster-Kronig transitions to $1s3p$ based states to radiatively contribute to the β^V feature. The $1s3s$ double ion and Rydberg states also contribute to the β^V complex.

The first triple excited neutral $1s3p^23d4s4p$ channel opens at about 46 eV above the $1s$ threshold. States based on the $1s3p^2$ configuration with two or three Rydberg electrons can also autoionize to states based on the $1s3p$ configuration.

A prominent absorption feature approximately 44 eV above threshold (labeled "G" in ref. 2 & 3) is in reasonable proximity to the calculated energies for $1s3p^24p^3$ and $1s3p^24s^24p$ neutrals with multiplet spreads of about 7.5 eV. Since it is in this energy region that the β'' feature begins to be evident, it is suggested that the correct origin of β'' is due to these triple vacancy states. This is supported by the observation that the $1s3s$ states which opened much less than 46 eV above threshold did not give rise to any β'' intensity. In addition these results support some preliminary theoretical predictions [4]. Additional theoretical work would be welcomed to give a more detailed description of the competing processes in these interesting spectra.

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This research has been funded in its entirety by the National Bureau of Standards.

X-24A ATOMIC PHYSICS: ENERGY DEPENDENCE OF THE $K\beta^V$ SATELLITE IN Ar GAS

T. Jach (NBS), P. L. Cowan (NBS), S. Brennan (SSRL), R.E. LaVilla (NBS), and R.D. Deslattes (NBS)

We have taken advantage of the high x-ray flux delivered by the X-24A beamline to measure the excitation energy dependence of the Ar $K\beta$ fluorescent line (3190 eV) and its two satellites. Previous work in this area [1] has called attention to the satellites of the Ar $K\beta_{1,3}$ line, which are designated $K\beta^V$ and $K\beta^H$. These satellite lines, occurring about 3.1 and 7.0 eV, respectively, above the $K\beta_{1,3}$ line, have been attributed to multiple vacancy states excited well above the Ar K edge [1,2].

We have taken extensive data on the intensities of the $K\beta^V$ satellites relative to the $K\beta_{1,3}$ line itself over an energy range of 0-200 eV above the K edge. Ar gas near atmospheric pressure was excited by the highly focussed x-ray beam produced at beamline X-24A. A combination of x-ray optics and a double crystal monochromator produced a beam with a bandwidth of 0.4 eV, tunable in energy about the Ar K-edge (3203 eV). Fluorescent radiation from the decay of the Ar excited states was analyzed by a bent-crystal focussing spectrometer of the Johann geometry and detected by a position-sensitive proportional counter of the backgammon type. The combination allowed us to record a spectral window 50 eV wide, including the $K\beta$ line and both of its satellites. We were able to monitor the absorption spectrum of argon as well, thus relating the turn-on of satellites in the fluorescence to various features associated with excited state series in the absorption. The figure below shows the behavior of the $K\beta^V$ satellite as a function of energy above the threshold.

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This research has been funded in its entirety by the National Bureau of Standards

X-24A ATOMIC PHYSICS: UNUSUAL THRESHOLD BEHAVIOR OF THE $K\beta^V$ FLUORESCENCE SATELLITE IN Ar GAS

T. Jach (NBS), P.L. Cowan (NBS), S. Brennan (SSRL), R.E. LaVilla (NBS), and R.D. Deslattes (NBS)

We have observed unusual threshold behavior in the $K\beta^V$ satellite of the $K\beta$ emission in fluorescence (3190 eV) from Ar gas, using the X-24A beamline. Previous work suggested that the $K\beta^V$ satellite originated from a shakeup transition to $([1s3p]4pnp)$ [1,2]. Recent calculations indicate [3] that the more likely assignment of this suprathreshold feature is the transition to $([1s]3p^53d^2)$. We have observed the amplitude and shape of this satellite as it is turned on at increasing energy. A series of spectra showing the $K\beta_{1,3}$ line and its $K\beta^V$ satellite for various incident energies above the threshold reveals a shoulder developing on the main line which then moves up in energy relative to the main line before becoming fixed and growing into a separate peak. In spectra taken over extended periods of time to obtain better statistics, the $K\beta^V$ satellite appears to have two components which may have different thresholds.

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This research has been funded in its entirety by the National Bureau of Standards.

B.H. McQuaide, D.E. Jenkins, M.D. Hawkins, M.S. Banna (Vanderbilt U.), P.L. Cowan (NBS), and B.A. Karlin (NSLS)

The $1s$ photoionization of argon has been studied with synchrotron radiation using beamline X-24A. At $h\nu=3600$ eV, the main shake up peak, which is probably due to $3p\rightarrow 4p$ excitation accompanying $1s$ ionization was found to be $10.8\pm 1\%$ of the main peak (see Fig. 1). This result has been shown to be close to the sudden limit value using the theory developed by Thomas [1]. It is somewhat higher than the ratios obtained by other workers, most of whom, however, used lower-energy photons. The multiconfiguration calculations of Dyall [2] also yield a smaller ratio of 7.1%.

Figure 1. The argon $1s$ spectrum obtained with 3600 eV photons at the magic angle.

Additional, higher resolution work is clearly needed on this system. It would then be possible to carry out a detailed comparison with theory.

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This work has been supported in part by the National Science Foundation (grant No. CHE-8319476) and by the National Bureau of Standards.

R.C.C. Perera (LBL); P.L. Cowan, T. Jach, R.E. Lavilla and D.W. Lindle (NBS); and B.A. Karlin (NSLS).

The Cl K absorption spectrum and Cl K β (K-V) fluorescent spectra of chloro-fluoro methanes were measured. The unoccupied molecular orbitals were selectively populated producing highly excited neutral molecules (i.e., exciton states), resulting in x-ray emission spectra from photon excitation below the ionization threshold [1]. As an example, results from CF₃Cl molecule are presented.

The Cl K absorption spectrum of CF₃Cl (gas) is shown in Fig. 1. The lowest unoccupied valence molecular orbitals (MOs) of CF₃Cl are 6a₁, 7a₁ and 6e in the order of decreasing binding energy (BE). The first discrete absorption maximum at 2823.1 eV results from transition of a chlorine 1s electron to the unoccupied 6a₁ orbital.

The Cl K β (K-V) emission spectrum presented in Fig. 2 was excited at 2832.5 eV energy, which is about 3 eV above the Cl 1s ionization threshold energy (K + 3 eV), but below the double vacancy threshold energy. It was shown before [1,2] that such excitation produces no multiple vacancy satellite contributions in this spectral region. Peaks A and B in Fig. 2 are assigned as dipole-allowed transitions from electrons in 5e and 5a₁ valence MOs, whereas peak C is attributed to the overlapping transitions from the 3e+2e+4a₁ valence MOs.

In Fig. 3, the Cl K β (K-V) spectrum excited with 2823.1 eV (K-6.5 eV) photon energy is presented, along with the deconvolved spectral components. As seen in Fig. 1, the 2823.1 eV energy corresponds to the first maximum in the absorption spectrum. Comparing the Cl K β (K-V) spectral components for (K - 6.5 eV) excitation with the spectral components for (K + 3 eV) excitation, large differences in energy positions, relative intensities and line widths are observed. The relative energy-position shifts and the significant intensity changes can be understood in terms of perturbation effects due to the presence of an electron in the first unoccupied MO [1].

When a core electron is excited to an unoccupied orbital below the vacuum level, the "effective" hole production region in the core state [3] is limited by convolution of the the broadening of the unoccupied level and the band pass of the monochromator (neglecting the core hole reorganization effects). Since this "effective" core hole region is a fraction of the total 1s lifetime broadening, the line width of x-ray emission components from the exciton state will be smaller than the line widths of the above-threshold excited spectrum.

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Fig. 1. Experimental Cl K absorption spectrum of CF₃Cl. The position of Cl 1s ionization threshold energy is indicated.

Fig. 2. The Cl K β (K-V) spectrum of CF₃Cl excited with 2832.5 eV photon energy along with the deconvolved Voigt spectral components.

Fig. 3. The Cl K β (K-V) spectrum of CF₃Cl excited with 2823.1 eV photon energy.

One of the authors (R.C.C.P.) acknowledges the support by the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

X-24A CHEMICAL PHYSICS: POLARIZATION OF X-RAY FLUORESCENCE FROM CH_3Cl .

D.W. Lindle, P.L. Cowan, R.E. LaVilla, T. Jach (NBS); B. Karlin (NSLS);
and R.D. Deslattes (NBS)

Monochromatic synchrotron radiation (SR) with a high degree of linear polarization from beamline X-24A was used to resonantly excite Cl K-shell electrons in CH_3Cl to the unoccupied $8a_1$ antibonding molecular orbital. The subsequent Cl $K\beta$ fluorescence was energy- and polarization-analyzed by a curved-crystal secondary spectrometer with excellent polarization selectivity. Two Cl $K\beta$ spectra for orthogonal fluorescence polarizations are shown in the figure, where peak C in each spectrum has been scaled to the same relative intensity. We observe that the $K\beta$ fluorescence is strongly polarized.

The direction of polarization is determined by the symmetry of the valence orbital involved in the fluorescence decay which fills the Cl 1s hole; valence orbitals of σ symmetry produce fluorescence x-rays polarized parallel to the SR polarization, whereas fluorescence from π -symmetry orbitals is polarized perpendicular to the SR polarization. Calculations [1] agree well with these observations, and indicate that, in CH_3Cl , the resonance lifetime is short enough to preclude substantial disorientation of the molecule prior to fluorescence decay. Measurements of this type may prove to be a sensitive probe of molecular-orbital symmetry in more complicated systems.

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This research has been funded in its entirety by the National Bureau of Standards.

X-24A CHEMICAL PHYSICS: POLARIZATION OF X-RAY FLUORESCENCE FROM CHLORO-FLUORO-METHANES

D.W. Lindle, P.L. Cowan, T. Jach, R.E. LaVilla (NBS), B.A. Karlin, (NSLS), and R.C.C. Perera (LBL)

Highly polarized x-ray fluorescence has been observed following K-shell excitation of several chloro-fluoro-methanes. Monochromatic synchrotron radiation (SR) with a high degree of linear polarization was used to resonantly excite Cl 1s electrons in CF_3Cl , CF_2Cl_2 , and CF_3Cl . The subsequent Cl K β fluorescence was found to be strongly linearly polarized (see figures).

The direction of polarization of the K β fluorescence is determined in part by the symmetry of the valence-orbital electron involved in the fluorescence decay which fills the Cl 1s hole. Our results illustrate that the core-level resonance lifetimes are short enough to preclude substantial disorientation of the molecule prior to fluorescence decay. Measurements of this type may prove to be a sensitive probe of orbital symmetry in more complicated molecular systems, condensed matter, and adsorbates.

The present measurements were performed at beamline X24-A at the National Synchrotron Light Source at Brookhaven. A high-energy-resolution primary monochromator focuses the incident beam into a cell containing the sample gas. The molecular x-ray fluorescence emitted upward from the gas cell is collected by a curved-crystal secondary spectrometer with position-sensitive detection. Polarization sensitivity is accomplished by using a Si(111) crystal in the spectrometer (and in the primary monochromator), for which the Bragg angle is 44.6° for Cl K β fluorescence. Rotation of the secondary spectrometer, and hence the crystal dispersion plane, by 90° suffices to detect orthogonal fluorescence-polarization components.

These preliminary results suggest the usefulness of fluorescence polarization to the assignment of resonant features both below and above threshold, and of the final valence-hole-state symmetry. Beyond this straightforward spectroscopic utility, more general applications might include the study of molecules, ions, or molecular fragments in different environments and phases to determine spectroscopic or geometrical parameters. Furthermore, we suspect that the atomic specificity of this phenomenon may permit its use to study adsorbate orientations on surfaces.

One of the authors (RCCP) acknowledges support by the U.S. Department of Energy (contract no. DE-AC03-76SF00098).

X-24A CHEMICAL PHYSICS: NEAR-RESONANT EXCITATION OF SULFUR X-RAY EMISSION FROM SULFUR HEXAFLUORIDE

P.L. Cowan, R.D. Deslattes, T. Jach, R.E. LaVilla, D.W. Lindle (NBS), and B.A. Karlin (NSLS).

Sulfur hexafluoride has long challenged the understanding of practitioners of core-level spectroscopies. The x-ray absorption spectrum is particularly rich in surprises and detailed structure [1, 2]. Recently, photoionization spectroscopy has yielded some clues to the origin of several of the supra-threshold absorption features [3]. We have initiated studies of the molecule using energy selective excitation of x-ray emission spectra, partially to check the assignment of the supra-threshold resonances and partially to study the subthreshold region. Preliminary analysis of our data appears to add to the mysteries of this molecule.

An example of the striking complexity observed by x-ray emission is presented in Fig. 1. When the incident x-ray energy is tuned to the lowest sub-threshold absorption resonance, four emission peaks are resolved near the S $K\alpha$ fluorescence energy. The two low energy peaks, labeled W & X, are anomalously broad (2.5 eV) while the higher energy doublet peaks, Y & Z, are significantly narrower (0.7 eV) than the observed supra-threshold $K\alpha$ fluorescence peak widths (1.0 eV). The positions of peaks W & X change linearly with changing excitation energy. Furthermore, comparison of polarization analyzed spectra indicates the peak W is strongly polarized. Finally, although the Y-Z doublet appears at the same emission energy as supra-threshold excited $K\alpha_{1,2}$ fluorescence, the relative amplitudes are reversed (i.e., Z is less intense than Y whereas normally the higher energy $K\alpha_1$ line is stronger).

Although this molecule may be somewhat "pathological" (i.e., atypical of molecular spectroscopy in general) it is important to accept the challenge of interpreting these results before one can have complete confidence in the use of core-level spectroscopies for studies of less exotic molecules.

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This research has been funded in its entirety by the National Bureau of Standards.

X-24A SOLID STATE SCIENCE: POTASSIUM AND CHLORINE K-ABSORPTION AND $K\beta$ FLUORESCENCE OF KCl

R.E. LaVilla, P.L. Cowan, D.W. Lindle (NBS); S. Brennan (SSRL); B. Karlin (NSLS); and R.D. Deslattes (NBS)

As a continuing part of our study of inner shell excitation phenomena, we measured the K-absorption and $K\beta$ emission from the KCl system, whose ions are isoelectronic with argon. The K and Cl $K\beta$ emission from a single crystal of KCl was obtained as a function of incident photon excitation through their respective 1s thresholds and extending to about 100 eV above the 1s edges.

These data provide information on the origin of the different features of the emission spectrum. Thus $K K\beta''$ and $Cl K\beta_x$ are due to the decay of a complex of initial double-vacancy states because they are absent within 10-15 eV above the 1s edge. However, near threshold the $K\beta_5$ feature persists. This observation supports the view of $K K\beta_5$ as a single-vacancy transition. Further, the alignment of the $K K\beta_5$ with $Cl K\beta_{1,3}$ relative to the respective K and Cl absorption features supports the designation of $K K\beta_5$ as a cross transition.

This research has been funded in its entirety by the National Bureau of Standards.

X-24A SURFACE SCIENCE: STRUCTURE OF Cl ADSORBED ON Cu(100) DETERMINED BY BACK-REFLECTION X-RAY STANDING WAVES

J. Rowe (Bell Labs), F. Sette (Bell labs), P.L. Cowan (NBS), T. Jach (NBS), and B.A. Karlin (NSLS).

The Cl/Cu(100) adsorbate system was studied as a test for the new back reflection x-ray standing wave technique. This system has been carefully studied by established techniques [1]. It also presents a challenge to the x-ray standing wave method in that previously x-ray standing wave studies of metal crystals was all but impossible.

The sample crystal was known to have a mosaic spread of $\approx 1/4^\circ$. Despite this a clear x-ray standing wave effect is observed in the back reflection geometry. The Cl adsorption site was 1.7 Å above the Cu(200) plane at the surface. Plots of the Cl K-fluorescence, the Cu LMM Auger and the diffracted beam intensity vs. incident x-ray energy are shown.

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X-24A SURFACE SCIENCE: STRUCTURE OF S ADSORBED ON Cu(100) DETERMINED BY SEXAFS AND BACK-REFLECTION X-RAY STANDING WAVES

F. Sette (Bell Labs), J. Rowe (Bell Labs), P.L. Cowan (NBS), T. Jach (NBS), and B.A. Karlin (NSLS).

We have studied the structure of sulfur adsorbed on a Cu(100) surface using a variety of techniques. In addition to conventional laboratory analysis techniques such as LEED and electron beam stimulated Auger analysis, we examined the structure with SEXAFS and the novel back-reflection x-ray standing wave method.

A Cu(100) surface was sputter cleaned and annealed to 450°C for 5 min. The sample was then exposed to H₂S and was annealed further at 200°C until a p(2x2)S/Cu(100) LEED pattern was observed. Sulfur coverage was approximately 1/2 monolayer.

SEXAFS was recorded by observing the S-fluorescence as a function of incident x-ray energy. The absorption spectrum and the derived pair distribution function are shown. Results indicate that the sulfur atoms sit at a 4-fold hollow site with a nearest neighbor (S-Cu) bond length of 2.24 Å. We believe that this is the first and only SEXAFS spectrum taken at the NSLS x-ray ring to date.

The sulfur adsorption site was also located by the back-reflection x-ray standing wave method. Both the Cu(200) reflection, normal to the surface, and a Cu<111> reflection were used. Preliminary analysis of the x-ray standing wave results indicate the sulfur atoms sit 1.6 Å above the Cu(200) plane at the surface.

X-24A SURFACE SCIENCE: TEMPERATURE DEPENDANCE OF SULFUR ADSORPTION SITE ON Cu(100)
STUDIED BY BACK-REFLECTION X-RAY STANDING WAVES

T. Jach (NBS), P.L. Cowan (NBS), F. Sette (Bell labs), J. Rowe (Bell Labs) and B.A. Karlin (NSLS).

The back-reflection x-ray standing wave technique was used to observe the structure of sulfur adsorbed on a Cu(100) surface as a function of crystal temperature. For this system a reversible phase change has been observed with LEED. At room temperature a $p(2 \times 2)$ LEED pattern is observed, but at 250°C the pattern changes to (1×1) .

The thermal expansion of the Cu substrate causes the energy where the back-reflection diffraction condition occurs to decrease. The figures compare the x-ray standing wave results obtained by observing the standing wave dependance of the S K-fluorescence at room temperature and at 400°C.

It is apparent that although the Cu-Cu bond-lengths are expanding, the S-Cu bond-lengths at the surface expand much faster with temperature. Preliminary analysis indicates that while the Cu-Cu bonds expand by about 1% the S-Cu bond-length increases by $\approx 25\%$. Measurements were also taken at 7 intermediate temperatures.

It is important to note that our results indicate the x-ray standing wave technique is capable of determining atomic structure at elevated temperatures where other structure techniques such as SEXAFS and LEED cease to yield meaningful results.

This research has been funded in its entirety by the National Bureau of Standards.

COMBINED LASER-SYNCHROTRON PHOTOEMISSION EXPERIMENTS ON X-24C

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The extension of photoelectron spectroscopy to the study of laser excited materials has begun on the NRL soft x-ray beam line with the installation of a copper vapor laser and time-resolved detection capability. Laser induced, pulsed photovoltages on clean silicon surfaces have been measured with 2 to 15 ns resolution by recording the transient Si 2p core level shifts. Such experiments yield information on the dynamics of the laser excited electron-hole plasma and its interaction with the surface.

The beam line terminates in a conventional ultra-high-vacuum surface science chamber equipped with a cylindrical mirror analyzer (CMA) for photoelectron detection. The copper vapor laser provides 20 ns pulses with a wavelength of 510 nm at a repetition rate of 6 kHz. Photoelectron arrival times, relative to the laser pulse, are recorded by a time-to-digital converter capable of processing up to eight events.

The measurements were taken in two modes. For time-resolved energy distribution curves, signal-to-noise considerations demanded that the ring operate in single bunch mode. In this mode, the copper vapor laser was synchronized to the x-ray pulse, and the best time resolution was realized. In the second mode, used for recording the photovoltage decay, the ring was operated in multibunch mode and the laser free-ran relative to the x-ray pulses. Here, the CMA was set to a kinetic energy near an inflection point on the core level line shape, and the count rate recorded as a function of time as the line edge shifted in response to the photovoltage. In this mode, time resolution was measured to be ~ 15 ns, limited by spread in photoelectron transit times through the CMA.

Si (111) n- and p-type samples were prepared by thermal desorption cleaning, by sputtering, or by sputtering and annealing. Several surfaces were also studied as a function of dosing with dissociated hydrogen. Spectra were recorded with both bulk ($h\nu = 107$ eV) and surface ($h\nu = 130$ eV) sensitivity. Further experimental details are contained in reference 1.

Except for those from sputtered-only surfaces, photovoltage decays compare qualitatively with a prediction, based on Johnson's treatment², in which surface state charge redistribution is neglected and the bulk electron-hole pair density is given by an analytic solution to the diffusion equation. In general, a large surface recombination is found, characterized by recombination velocities up to 10^6 cm/s. Photovoltages from hydrogen dosed surfaces match most closely the predicted decay. It is possible that the metallic surface state on the Si (111) 7x7 surface, which is severely attenuated with hydrogen dosing, plays a role in non-equilibrium surface charge redistribution which may account for the deviations from the predicted decay seen on clean surfaces. However, since large surface recombination is for the most part sustained on the hydrogen dosed surfaces, the metallic surface state is not primarily responsible for the large surface recombination. The long (> 60 μ s) photovoltage decays observed on sputtered-only surfaces are presumably caused by long-lived traps related to disorder.

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SYNCHROTRON MICROPROBE AND MICRO-OPTICAL STUDY OF GOLD IN CARLIN-TYPE ORES

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Site specific occurrences of gold in unoxidized Carlin-type ores [1] have been determined using combined micro-optical and synchrotron x-ray fluorescence (SXRF) microprobe techniques [2]. Knowledge of the gold sites and their mineral associations is important for understanding the genesis of these disseminated Carlin-type deposits, and in the exploration and recovery of gold from such deposits, currently the major commercial source of gold in the United States.

To date three unoxidized and two oxidized samples from the Carlin and Horse Canyon mines have been studied. Beamline X26 at the NSLS was used to achieve beam sizes down to 20 micrometers and SXRF minimum detection limits for Au from 3 ppm (in pyrite) to less than 1 ppm (in siliceous matrix) [3]. Following the location of Au-enriched areas in the samples using SXRF, high resolution SEM augmented with EDX analysis was used to identify and study the mineral components in the samples. EPMA was also used to analyze various mineral phases.

Initial results indicate that: 1) gold is not associated with pyrite of any size, contrary to earlier reports [4]; 2) gold is not associated with carbonaceous matter; 3) gold occurs sporadically in reticulated replacement quartz and secondary chert-like patchy quartz of early stages of silicification; and 4) gold is concentrated in matrix areas of pre-existing illite. Further studies are underway.

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Acknowledgements

Research supported in part by the NSLS/HFBR Faculty Student Support Program funded by DOE, and in part by DOE, Division of Chemical Sciences (Contract No. DE-AC02-76CH00016).

FY 1987 RESEARCH ACTIVITIES ON THE X-26 BEAM PORT

K. W. Jones, B. M. Gordon, A. L. Hanson, B. M. Johnson, M. Meron, J. G. Pounds (BNL), J. V. Smith, M. L. Rivers, S. R. Sutton (U. of Chicago)

Introduction

The activities at the X-26 beam port center on two main areas of research. First, new analytical techniques are developed¹ and used for experiments in geochemistry,² cosmochemistry³ and biomedical sciences.⁴ Second, the properties of very low-energy multiply-charged atoms are investigated in several ways.⁵ The activity at the X-26 beam line summarized here includes work done by the main BNL and Chicago groups as well as collaborators and users.

Beam Line Development

The configuration of the X-26C beam line is being changed during the shutdown of the x-ray ring. A completely new beam line is being added at the X-26A position.

On the X-26C line a 1:1 focussing mirror is being installed to increase the flux of the white-light beam. A monochromator is being added so that monoenergetic photons can be used. Changes in the beam line vacuum system are being made so that it can be operated in the windowless mode. This change will eliminate the low-energy cut-off in the energy spectrum caused by the beryllium windows previously used to isolate the beam line from the ring vacuum system. The X-26A line will be equipped with a focussing mirror designed to produce a demagnification of the source by a factor of eight. The intent is to provide a maximum flux of photons in the hutch to be used for x-ray microscopy experiments.

Analytical Technique Development

Application of the x-ray fluorescence technique to trace element detection was pursued with the objectives of developing maximum sensitivity and lateral spatial resolution. Two types of instruments were used to produce a photon beam with dimensions of about 10 μm . One instrument used a collimated beam and the other a focussed beam. Lateral resolutions of 10 micrometers and minimum detection limits close to one femtogram were obtained.

Work on the development of micro-computed tomography methods was successful in obtaining a spatial resolution of 30 micrometers. One aim of the project is to use the technique for *in-vivo* diagnostics on experimental animals. This was accomplished for the first time during the last year when the head of an anesthetized mouse was successfully imaged.

Atomic Physics

An extensive study of multiply-charged argon ions produced by photoionization was carried out. Measurements were made of fluorescent radiation emitted in the process, argon ions with a charge up to 8+ were trapped at an energy of 40 meV and used for rate coefficient determinations, and molecular effects were demonstrated in the energy spectrum of the ions extracted from the production region.

Geochemistry and Cosmochemistry

The results of experiments done during the past year show that the synchrotron x-ray microscope is a unique tool for the characterization of the elemental content of the materials encountered in cosmochemistry and geochemistry. They demonstrate that the combination of good spatial resolution, low values for the minimum detection limits, and ease of quantitation give the synchrotron instrument special properties when compared to electron or ion probes.

Biomedical

Experiments were done that evaluated the distribution of essential trace elements in cerebrum, cerebellum, kidney and liver, of a toxic element (lead) in bone and cerebrum, and of metal containing drugs in normal and tumorous tissue.

¹Processes and Techniques Branch, Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

²National Science Foundation Grant No. EAR8313682 to the University of Chicago.

³Grant No. NAG 9-106 to the University of Chicago.

⁴The beam line operates as a NIH Biotechnology Research Resource under Grant No. P41RR01838.

⁵Fundamental Interactions Branch, Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

REGIONAL ALTERATIONS IN TRACE ELEMENT CONTENT IN BRAINS OF LEAD-EXPOSED RATS¹

S. M. Lasley (U. of IL Coll. of Med.) and J. G. Pounds (BNL)

Animal models of chronic lead exposure have been employed to produce environmentally relevant levels of the metal in blood (30-40 µg/100 ml) in order to study its actions on CNS function. A few such studies have also measured lead content either in whole brain (1,2) or brain regions (3) to correlate with blood lead levels and length of exposure. No attempts have been made however to examine the effects of chronic lead exposure on brain content of other trace elements that play important roles in neuronal function such as calcium, iron, and zinc. Therefore, this study was performed to investigate the effects of chronic lead exposure on content of trace elements in specific brain regions.

Long-Evans hooded rats were mated and on day 14 of gestation switched to NIH-07 diet to maintain a more consistent mineral intake. At parturition dams received 0.2% lead acetate in their drinking water, thus exposing the suckling pups to lead via the maternal milk. Control dams were maintained on distilled water. Offspring were weaned to and maintained on the same solution given their dam until sacrifice at 90 days. Brains from five exposed and five control rats were sliced by microtome in coronal sections 20 µm thick in a cryostat at -15°C, and slices appropriate for the visualization of nucleus accumbens, caudate-putamen, substantia nigra, ventral tegmental area and hippocampus were placed on Kapton film. Adjacent sections were placed on glass slides and treated with a hematoxylin and eosin stain to aid in anatomical identification. Samples were analyzed using synchrotron microprobe radiation from the 2.5 GeV light source. Sections were placed at 45° to the beam (200 µm square spot) and the resulting x-ray spectra collected at 90° by a Si(Li) detector using a 150 µm aluminum filter on the primary beam and a 100 µm Kapton filter on the detector. Spectra were fitted using a modified version of HEX, a curve-fitting program, on a MicroVAX II computer. Elemental concentrations are calculated from a detector efficiency curve obtained from gelatin standards spiked with selected trace elements and mounted on Kapton. Multiple point measurements were also taken to characterize the five brain areas of interest.

Initial data analysis indicated that manganese and iron were significantly decreased in ventral tegmental area of rats chronically exposed to lead ($p < 0.05$). Iron is an important cofactor for enzymes involved neurotransmitter synthesis, but it is not known what proportion of the decrease in content is due to iron of heme origin. Previous studies have shown that this exposure protocol does not alter hemoglobin or serum iron. Irrespective of treatment, calcium and manganese (both $p < 0.01$) as well as copper and zinc (both $p < 0.05$) differed significantly across brain regions. Lastly, the method did not have sufficient sensitivity to quantify lead content, which previously has been determined in whole brain analyses with this exposure model to be about 400 ng/g tissue in exposed animals (1). Further data analysis is currently being conducted.

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¹This work was supported by NIH grant ES04359 and the NSLS.

SECTION 4

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