

MAPPING IMPURITY ATOMS WITH X-RAY STANDING WAVES

X-ray and neutron diffraction have long been powerful techniques in crystallography, but they suffer from a serious drawback. Although scattering amplitudes can be measured with precision, information about the phase of the scattered radiation is lost. This phase ambiguity means that the scattering data cannot be simply Fourier transformed into a map of atom locations. Instead, complex statistical methods must be used to retrieve the phase information and extract the crystal structure. Atomic fluorescence emitted during excitation of an x-ray standing wave provides a powerful alternative because phase information can be retained. Recently, researchers at Argonne National Laboratory, Northwestern University, and the University of Illinois at Chicago used this technique to locate impurity atoms in the crystal lattice of muscovite.

X-ray standing waves are created in a crystal when an incoming beam is reflected by Bragg planes in the lattice, much like the standing wave in an organ pipe. Atoms in this standing wave field will then emit characteristic fluorescence radiation that allows identification. Because this characteristic emission signals both phase and amplitude, these data can be Fourier transformed back to a real-space atomic distribution. For the present experiment, the research team examined the distribution of manganese, iron, titanium, and barium impurities in a sample of muscovite mica, whose native atomic constituents are potassium, silicon, and aluminum.

The research team used x-rays from the BESSRC/XOR beamline 12-ID-D at the APS. A silicon monochromator selected the beam's energy to 7.44 keV, and additional beam conditioning was provided by two postmonochromators. Characteristic atomic fluorescence was collected at a grazing angle above the sample surface plane and analyzed with a solid-state detector. X-ray standing wave data were taken for the first eight orders of Bragg reflection. For each Bragg order, the sample was rotated through the Bragg reflection to shift the standing wave pattern to modulate the atomic emission yield. In this experiment, phase data were obtained via dynamical diffraction theory and known structure factors for muscovite. The amplitude and phase data could then Fourier inverted to create the real space representation.

The researchers found that the distributions of lattice cations obtained by the standing wave method quantitatively reproduced the known structure of muscovite (Fig. 1). In this study, the known muscovite scattering structure factors were used in analysis of the fluorescence yield. But even if the bulk structure is not available, it should be possible to make use of the precision reflectivity measurements to iteratively invert the data without reference to *a priori* structural information. Although more complex, such an inversion would produce a completely model-independent distribution of lattice atoms.

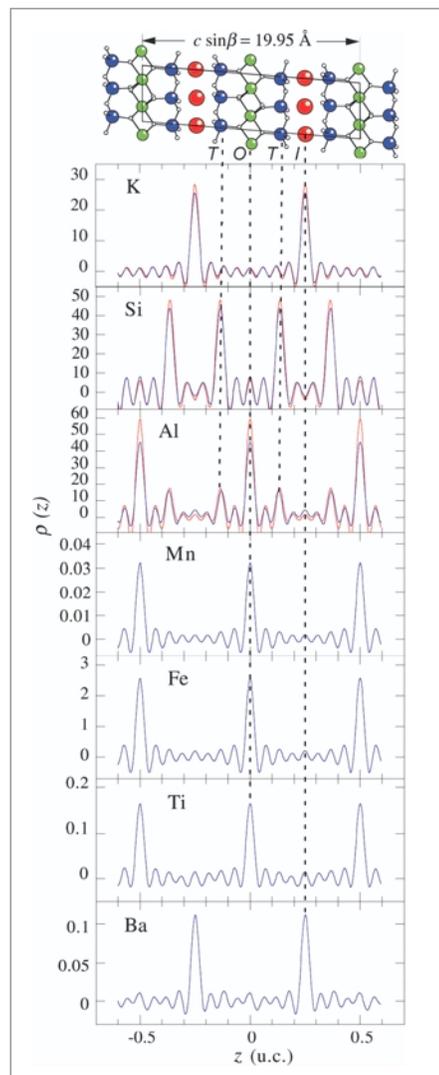


Fig. 1. Distributions of lattice atoms (K, Si, Al) and impurity atoms (Mn, Fe, Ti, Ba) in the muscovite unit cell. Blue lines show distributions based on Fourier solution of x-ray standing wave data. Red lines indicate lattice atom distributions similarly derived from crystallographic data. Diagram at top shows unit cell model on same scale as distribution data. Interlayer, tetrahedral, and octahedral sites are red, blue, and green, respectively.

To demonstrate the feasibility of the model-dependent approach, the research team obtained the density distributions of the impurity atoms Mn, Fe, Ti, and Ba. The results show that while Mn, Fe, and Ti occupy octahedral (Al) sites, the Ba impurities are found at interlayer positions (K sites).

X-ray standing wave methods such as those demonstrated in this work provide an alternative to conventional diffraction techniques, particularly if element-specific density distributions are desired. In the future, x-ray standing wave structural data

are expected to be especially useful in complex bulk-impurity measurements and surface chemistry studies. Moreover, these results indicate the value of high-brightness facilities, such as the APS synchrotron, in successfully carrying out x-ray standing wave measurements. ○

See: L. Cheng¹, P. Fenter¹, M.J. Bedzyk^{1,2}, and N.C. Sturchio^{1,3}, "Fourier-Expansion Solution of Atom Distributions in a Crystal Using X-ray Standing Waves," *Phys. Rev. Lett.* **90**(25), 255503-1 to 255503-4 (27 June 2003).

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REVEALING FINE DETAILS OF GOLD NANOPARTICLES

A major challenge in the study of nanometer-scale particles is their tendency to behave unpredictably: they aggregate, or clump together, and nucleate, or disperse. One way to achieve a degree of stability and homogeneity is to cap the particles with a molecular agent that acts at the surface of the particle to control the size. This allows more precise exploration of the structure and electronic properties of nanoparticles.

By using an array of probes, including high-energy spectroscopy at the PNC/XOR 20-BM and 20-ID beamlines at the APS, and the Canadian Synchrotron Radiation Facility (CSRF) at the Synchrotron Radiation Center (SRC), University of Wisconsin-Madison, researchers from the University of Western Ontario conducted a systematic study of the structural and electronic characteristics of gold nanoparticles. In these studies, the capping agent thiol was used to manipulate and control the size of the nanoparticle, and high-beam probes measured changes in the surface electronic charge and crystal structure of the particles as the size decreased.

First, by manipulating the ratio of the gold salt and the capping agent at 0°C, a degree of control was achieved in synthesizing gold nanoparticles ranging in size from 1.6 to 4.0 nanometers.

Extended x-ray absorption fine structure (EXAFS) analysis revealed that the structure of the gold nanoparticles did indeed change as size varied. In the smaller nanoparticles, the atoms in the lattice contracted relative to bulk as the size decreased. This confirms and further refines the results of electron microscopy probes. Measurements of the x-ray absorption coefficient of the particles also revealed that as the size decreased, the EXAFS oscillations were broader and less intense, though the pattern remained intact, suggesting that the smaller particles become more disordered and the nanoparticle remains crystalline.

Probes of the electronic characteristics of the nanoparticles by using x-ray absorption near-edge structure (XANES) analysis showed that the electronic charge of the thiol-capped nanoparticles was depleted in the smaller particles (Fig. 1).

The capping molecule alkanethiolate also affected the electronic properties of the nanoparticles. Naked or weakly capped nanoparticles generally contract relative to the bulk. However, analysis with x-ray absorption fine structure (XAFS) detected a slight reduction in the contraction of thiol-capped particles.

XANES analysis supported a previous observation, inferred from measuring the intensity of the x-ray whiteness, that there is some transfer of electronic charge from the gold nanoparticle to the thiol capping agent. XANES analysis also

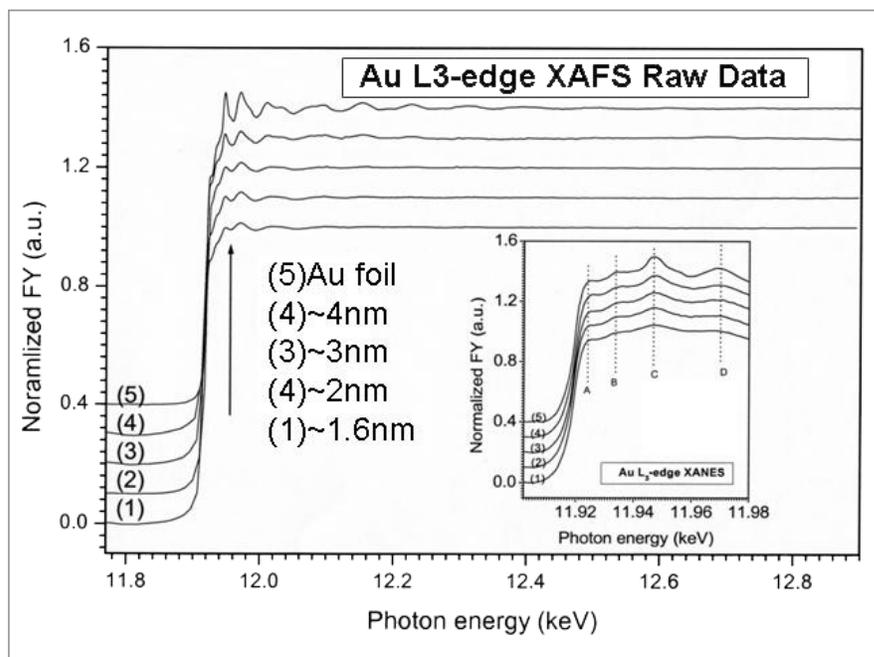


Fig. 1. Raw data obtained at the APS show the trend of the absorption spectrum as a function of size. The arrow indicates the similarities of spectra as size increases. As the particles become larger, the features are better defined. The inset shows the threshold of absorption where the x-ray has sufficient energy to take one electron from a $2p_{3/2}$ to a higher level of gold 5 d character above the Fermi level.

was used to determine whether the interaction of the bonding agent sulfur/thiol was sensitive to size. Previous studies had suggested a weak correlation with size, and this analysis supported that finding, revealing only a slight increase in bonding strength for the smallest 1.6-nanometer nanoparticles.

This systematic study of the properties of gold nanoparticles demonstrates that it is possible to gain a degree of control over the size and stability of nanoparticles and, with the help of high-intensity x-ray beams, obtain a more detailed understanding of the fundamental properties of these building blocks for the next generation of nanotechnologies. ○

See: P. Zhang and T.K. Sham, "X-ray studies of the structure and electronic behavior of alkanethiolate-capped gold nanoparticles: The electronic interplay of size and surface effects," *Phys. Rev. Lett.* **90**(24), 245502-1 to 245502-4 (2003).

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CRACKING OPEN A GLASS PUZZLE

With the right stimulus, some materials can make a transition from a low-density amorphous form to a higher density one. Though long known, this phenomenon of polyamorphism is not well understood. Part of the solution to this mystery lies in untangling the changes in atomic order over various length scales. Glasses, for example, can exhibit short-range order, which involves correlations between nearest neighbors. But ordered correlations beyond this can also exist, especially in network-forming glasses, and are generally known as intermediate-range order correlations. During transitions among amorphous forms, changes occur in both short-range and intermediate-range order. The former tend to be more straightforward, while the latter have become the subject of intense debate. Recently, a collaboration of researchers from the University of Wyoming, Argonne National Laboratory, Arizona State University, and the Centre de Recherche sur les Matériaux à Haute Température, in Orléans, France, has used x-ray and neutron diffraction to reveal the mechanism by which important structural changes occur in the glassy network before a polyamorphic transition in GeO_2 .

Canonical network glasses, such as GeO_2 and SiO_2 , both consist of corner-shared tetrahedra that link together to form cage structures. Likewise, both these systems undergo a polyamorphic transition under pressure. The structure of these materials becomes more compact as the coordination gradually changes from fourfold to sixfold. When pressure is removed, the coordination returns to fourfold but the density of the glass is found to be permanently increased, giving important clues to the mechanism of densification. Compaction results in a decrease of intermediate-range order and reduction in size of the network cages. In glassy GeO_2 this is also associated with a decrease in Ge-O-Ge bond angle with only a slight elongation of the Ge-O bond length. Previous neutron studies are subject to the problem of overlapping correlations, making it impossible to obtain exact details on the Ge-Ge distances. With a combination of neutron and x-ray scattering, new experiments at the APS have been able to highlight the salient structural transformations in densified GeO_2 .

In the current work, samples of GeO_2 were synthesized by a sol-gel process and annealed at 1400°C for 12 hours. The resulting glass was densified at room temperature in a 10-gps diamond anvil cell at Arizona State University. The sample's density increased by 11% and was observed to be stable during the two-year study. Neutron diffraction measurements were performed at the Intense Pulsed Neutron Source at Argonne National Laboratory, and the x-ray scattering was carried out at the BESSRC/XOR beamline ID-11-C at the APS. Taken together, the neutron and x-ray data make it possible to obtain difference structure factors, with each partial structure factor (Ge-Ge, O-O, and Ge-O) eliminated.

From previous studies, it has been long believed that the cation-cation correlations (Ge-Ge) were primarily responsible for the changes in intermediate-range order observed after densifi-

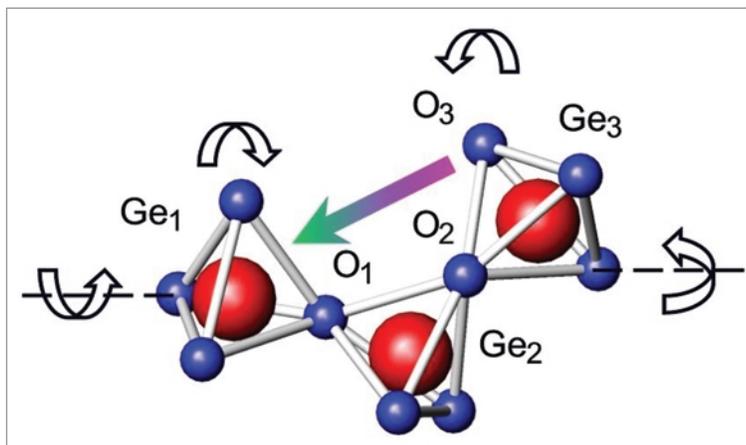


Fig. 1. Mechanism for GeO_2 densification proposed on the basis of combined neutron and x-ray diffraction studies. (Oxygen atoms are blue, germanium atoms are red.) Oxygen-oxygen correlations were found to be the most important factor in the changes in intermediate range order accompanying densification. The decrease in next-nearest neighbor oxygen distance is likely the result of rotation of the GeO_4 tetrahedra around the Ge-O-Ge bonds.

cation. But the difference structure factors obtained here show that the structural changes are greatest when the Ge-Ge correlations are eliminated and least when O-O correlations are factored out. Given the accepted picture of a network of corner-shared GeO_4 tetrahedra, the most likely explanation is that the tetrahedral units are rotated about the Ge-O-Ge bonds during densification and undergo slight distortion at the same time (Fig. 1).

These results have resolved the complex puzzle of how the network collapses, leading up to a polyamorphic transition in a classic network glass. Because the experiments required accurate data across a wide range of momentum transfers only achievable with high-energy x-rays, they also demonstrate the importance of third-generation synchrotron sources in making such studies feasible. In future, it should be possible to do *in situ* measurements on an absolute scale and follow the details of changes in glass structure all the way through the amorphous transitions. ○

See: S. Sampath^{1,2}, C.J. Benmore², K.M. Lantzky¹, J. Neuefeind², K. Leinenweber³, D.L. Price^{2,4}, and J.L. Yarger¹, "Intermediate-Range Order in Permanently Densified GeO_2 Glass," *Phys. Rev. Lett.* **90**(11), 115502-1 to 115502-4 (21 March 2003).

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A DASH OF TELLURIUM SMOOTHES THE WAY TO MORE ORDERLY FILMS OF GERMANIUM ON SILICON

Sandwich a little germanium between layers of silicon, and you've got yourself the heart of a high frequency transistor—if you can keep the germanium film smooth and regular on atomic scales. That's tricky because germanium and silicon atoms naturally arrange themselves in crystal lattices with slightly different spacings. However, as materials scientists from Northwestern University recently found, a dash of tellurium promotes orderly growth.

The atoms in both silicon and germanium fit into diamond structure lattices, and, in principle, it's possible to put down layers of germanium atoms that line up perfectly with the atoms in the silicon substrate, a process called epitaxial growth. However, germanium atoms naturally space themselves about 4% farther apart than silicon atoms, so the atoms in the germanium film are squeezed together horizontally. To compensate, they push farther apart vertically. After just a few layers of growth, the germanium atoms begin to rearrange to relieve the strain, and such “relaxation” creates defects in the film and can even cause the germanium to collect in little islands. The germanium and the silicon from the cap layer may also diffuse into each other, blurring the material interface, which, for most device applications, should be sharply defined.

Mixing in traces of arsenic, antimony, bismuth, or tellurium helps quell the unruliness by tying up the dangling chemical bonds on the surface as the film grows. For example, a little tellurium inhibits island formation and makes it possible to lay down hundreds of atomic layers of germanium one at a time, although such thick films are still riddled with defects. Now the Northwestern team has shown that tellurium also promotes the growth of strained, defect-free films up to nine layers thick. The tellurium atoms also inhibit the germanium atoms from migrating into the silicon cap, thus creating an atomically sharp interface. To prove it, the researchers employed a pair of x-ray techniques that revealed the atomic-scale structure of germanium films grown on a silicon (001) surface and capped with more silicon.

The team studied the vertical distribution of germanium by using x-ray standing waves in experiments at the DND-CAT beamline 5-ID-C at the APS and the National Synchrotron Light Source beamline X15A. Monochromatic x-rays diffracted off lattice planes in the silicon substrate, and the incident and diffracted beams interfered to create a standing wave that permeated the germanium above and caused it to fluoresce.

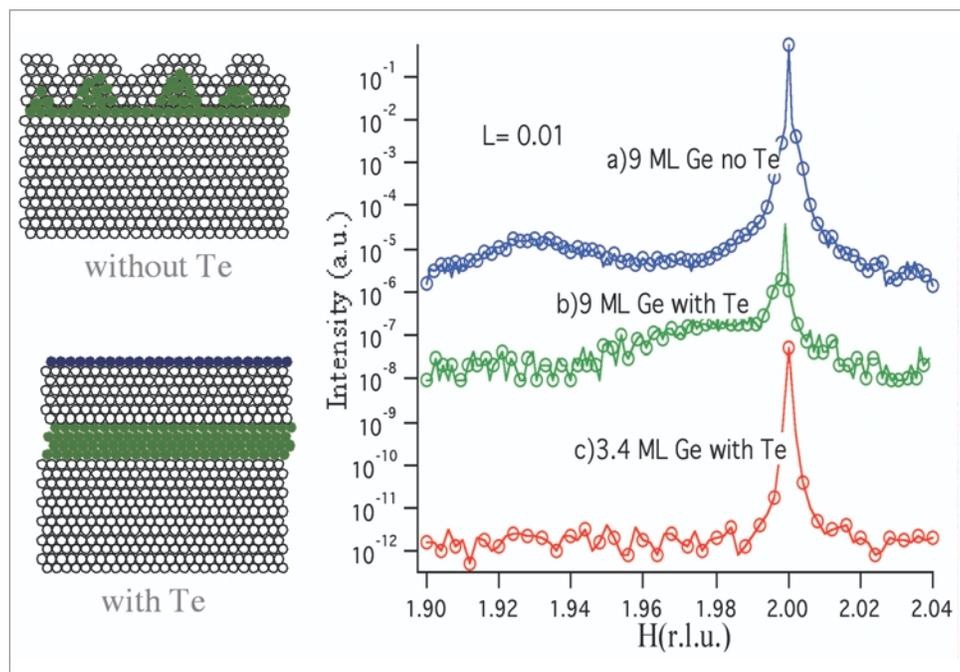


Fig. 1. Grazing incidence x-ray scattering data for a 70-Å Si/9 mono-layer (ML) Ge/Si(001) heterolayer structure grown by molecular beam epitaxy with and without a Te atomic layer being used as a surfactant. These are HK scans at $H = K$ and $L = 0.01$, at which the probed depth should be approximately 100 Å. The peak at $H = K = 2.00$ corresponds to the Si(220) Bragg peak. a) For the 9 ML Ge/ no-Te GIXD scan, there is evidence of fully relaxed Ge with the peak showing up at $H = K = 1.92$. b and c) This does not appear when Te is used as a surfactant. (Each set of data is vertically offset for reasons of clarity.) The left side depicts the side view of the resultant morphology for heterolayer structure. Ge/Si intermixing and islanding occur when Te is not used as a surfactant.

Researchers scanned the angle of the incident x-rays through the diffraction condition, which moved the planes of maximum intensity through the germanium and revealed the distribution of the material. Measurements around several diffraction peaks showed that for films grown in the presence of tellurium, germanium up to nine layers thick remained defect free. Without the tellurium, films just 3.7 layers thick relaxed and formed defects.

The researchers next studied the horizontal distribution of the germanium at the DND-CAT beamline by using a technique known as grazing incidence x-ray diffraction (GIXD). A beam of x-rays struck the sample at an angle so glancing that it could not penetrate deep into the silicon but was almost completely reflected. The beam could still probe the surface of the sample, however, and diffract off lattice planes lying perpendicular to it like a dominoes standing on end. The diffraction measurements showed that for films as thick as nine layers grown with

tellurium, the germanium atoms had the same horizontal spacing as the silicon atoms. But in a nine-layer film grown without tellurium, some of the germanium had relaxed to its usual, looser spacing.

The results show that tellurium impedes the movement of germanium atoms in the accumulating film, inhibiting relaxation and promoting the growth of orderly films. In theory, tellurium should be more effective than arsenic, antimony, or bismuth in smoothing germanium growth, as a single tellurium atom will tie up all the loose bonds from a silicon or germanium atom. It takes a pair of arsenic, antimony, or bismuth atoms to do the same thing. Bolstered by their smooth progress so far, the researchers hope to use tellurium to make thicker defect-free films. ○

QUANTUM LAYERING IN THIN METAL FILMS

Advances in nanotechnology critically depend on understanding the behavior of matter on an atomic scale. As the size of a structure decreases, its properties are increasingly influenced by the nonclassical rules of quantum mechanics. Of particular interest is the question of how thin films grow during atomic deposition onto a substrate. Theory predicts that quantum effects will control the morphology and thickness of the thin films as they grow, but experimental observations of this process have been difficult to obtain. Recently, researchers from the University of Illinois at Urbana-Champaign have used UNI-CAT beamline 33-ID at the APS to form a detailed picture of the growth of thin films of lead.

In metal films, electronic effects are important, and for thicknesses of one to several monolayers, quantum size effects are expected to play a dominant role. One direct manifestation of these effects will be variations in the atomic interlayer spacing as a function of the number of layers. Previous studies have attempted to measure step heights by means of scanning tunneling microscopy and helium atom scattering, but such methods are sensitive only to the topmost layer of the metal films. In the present work, x-ray specular reflection was used to precisely measure changes in the film structure for a wide range of thicknesses.

The samples were prepared by depositing lead vapor from an effusion cell onto a freshly prepared Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) reconstructed surface maintained at a temperature of 110K. Films were built up incrementally, and their structures were analyzed with each full completion of a new atomic layer. The extended x-ray reflectivity was measured at the 33-ID surface x-ray diffraction station. The incident beam energy was 19.9 keV, and the scattered x-rays were collected with a scintillation point detector. The background-subtracted integrated intensity for coverages of 6 to 18 monolayers are shown in Fig. 1.

Multilayer interference fringes appear in the reflectivity plots between the large silicon (111) and (333) Bragg peaks at reciprocal lattice units 3 and 9, respectively, and the smaller lead (111), (222), and (333) Bragg peaks at $l = 3.3$, 6.6, and 9.9, respectively. In the figure, inverted triangles mark the positions of prominent fringes at $l = 4.8$ and 8.1, which are half-

See: B.P. Tinkham, D.M. Goodner, D.A. Walko, and M.J. Bedzyk, "X-ray studies of Si/Ge/Si(001) epitaxial growth with Te as a surfactant," *Phys. Rev. B* **67**(3), 035404-1 to 035404-6 (15 January 2003).

Author affiliation: Northwestern University

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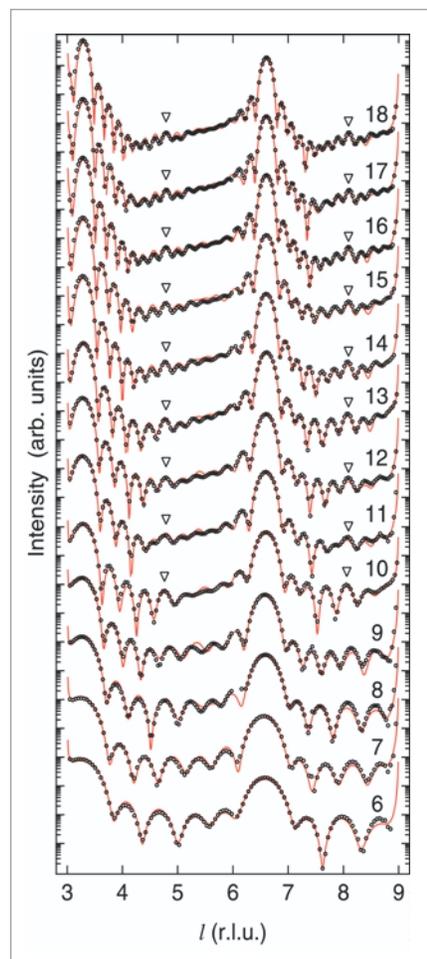


Fig. 1. Extended x-ray reflectivity for lead thin films with thicknesses from 6 to 18 monolayers. Open circles are the measured data. Solid red lines are fits to calculated reflectivity patterns based on lattice distortions derived from charge density variations in a quantum well. Inverted triangles indicate positions of prominent half-order features originating from quasibilayer periodicity. (r.l.u. = reciprocal lattice unit).

order features arising from a quasibilayer periodicity in the layer structure. These features are a direct consequence of quantum confinement of the electrons in the lead film, and they are accurately reproduced by a model of charge density variations in a one-dimensional quantum well structure. Charge imbalances cause the atomic layers to be shifted from their ideal bulk positions in an alternating fashion, leading to an effective near-doubling of the unit cell periodicity and the prominent interference fringes halfway between the lead Bragg peaks. As a further test, the researchers found that these results are also consistent with previous scanning tunneling microscopy and atomic scattering data.

A key finding of this work is that quantum confinement on an atomic layer scale can cause structural alterations that extend throughout a film, a phenomenon that must be understood in the application of metal films to nanotechnology. In addition, the ability to obtain these kinds of details of nanolayered materials at atomic resolution also shows the power of third-generation synchrotron facilities such as the APS. Future studies will investigate the effects that quantum confinement

can have on other film properties, including stability and relative surface energy. ○

See: P. Czoschke, H. Hong, L. Basile, and T.-C. Chiang, "Quantum Oscillations in the Layer Structure of Thin Metal Films," *Phys. Rev. Lett.* **91**(22), 226801-1 to 226801-4 (28 November 2003).

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SOFT GRAPHITE BECOMES SUPERHARD UNDER HIGH PRESSURE

Carbon exhibits a rich structural chemistry because of its ability to form linear (sp), trigonal (sp^2), and tetrahedral (sp^3) hybridized bonds. Recent successes in synthesizing new forms of carbon have stimulated considerable theoretical and experimental interest in synthesizing new allotropes. The processes that initiate and govern these transformations are only beginning to be understood, despite their great scientific and technological importance.

In the transformation of graphite under cold compression, there is a marked increase in electrical resistivity above 15 GPa, a sharp drop in optical reflectivity, broadening of the pure-graphite E_{2g} Raman line from 9 to 15 GPa, an increase in optical transmittance above 18 GPa, and changes in x-ray diffraction patterns beginning at 14 GPa. These observations have led to speculations that the high-pressure phase may be a hexagonal diamond phase, an intermediate phase between graphite and diamond, or an amorphous phase.

Researchers from The University of Chicago, the Carnegie Institution of Washington, Brookhaven National Laboratory, Argonne National Laboratory, and the University of Alaska performed a direct characterization of the π and σ bonding of compressed graphite by using synchrotron-based inelastic x-ray scattering (IXS) spectroscopy. They ground a single-crystal graphite sample into a fine polycrystalline aggregate and loaded it into a diamond anvil cell (DAC). Under uniaxial com-

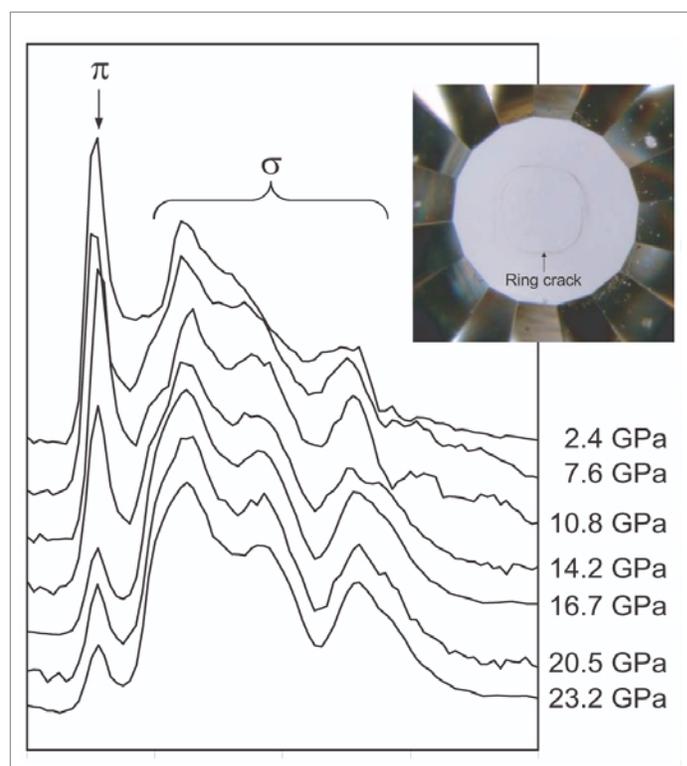


Fig. 1. IXS spectra for compressed graphite plotted as normalized intensity (i.e., scattered intensity normalized to the incoming intensity) versus energy loss (incident energy minus analyzer energy). The spectra were taken in the vertical direction, which probes the c plane. The lower energy peak corresponds to transitions associated with π bonding and the higher energy portion corresponds to transitions associated with σ bonding. After the transition at ~ 17 GPa, the σ bonds increase at the expense of the π bonds. The insert shows a photomicrograph of the indentation of a diamond anvil by the compressed, superhard graphite sample.

pression, the polycrystalline graphite sample quickly developed a strong preferred orientation, so IXS spectra for specific crystallographic directions were obtained by repeatedly reorienting the DAC.

To investigate structural changes in the sample while avoiding the complication of a strong preferred orientation and peak broadening due to uniaxial stress, the researchers conducted an x-ray diffraction study to 24 GPa by using a helium hydrostatic medium. Monochromatic x-radiation at 37.45 keV gave rise to diffraction patterns that were collected with a charge-coupled device detector at the GSECARS 13-BMD beamline; the results were subsequently confirmed at the HP-CAT 16-ID-B beamline at the APS.

Graphite was found to undergo a transition at ~ 17 GPa when compressed under ambient temperature. The near-K-edge spectroscopy of carbon using synchrotron-based IXS revealed that half of the π bonds between the graphite layers converted to σ bonds, whereas the other half remained as π bonds in the high-pressure form (Fig. 1). The x-ray diffraction pattern of the high-pressure form was consistent with a distorted graphite structure in which bridging carbon atoms between graphite layers pair and form σ bonds, while non-bridging carbon atoms remain unpaired with π bonds.

The new phase exhibited exceptional hardness (see insert in Fig. 1). After releasing the pressure on the high-pressure phase (without the helium pressure medium), the researchers

found that the graphite sample had left a ring crack indentation on the diamond anvils that traced the original boundary of the sample. In normal DAC operation, ring cracks have been observed only when a diamond anvil is indented by another superhard material, such as an opposing beveled diamond anvil. The reversible, orders-of-magnitude change in strength from very soft graphite to a superhard material offers the possibility of intriguing applications, such as uses as a pressure-dependent structural component (for instance, a composite gasket for a high-pressure apparatus). ○

See: W.L. Mao^{1,3}, H.-k. Mao^{1,3}, P.J. Eng^{1,2}, T.P. Trainor^{2,6}, M. Newville², C.-c. Kao⁴, D.L. Heinz¹, J. Shu³, Y. Meng⁵, and R.J. Hemley³, "Bonding Changes in Compressed Superhard Graphite," *Science* **302**(17), 425-427 (October 2003).

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NEW OPPORTUNITIES FOR ACTINIDE SCIENCE

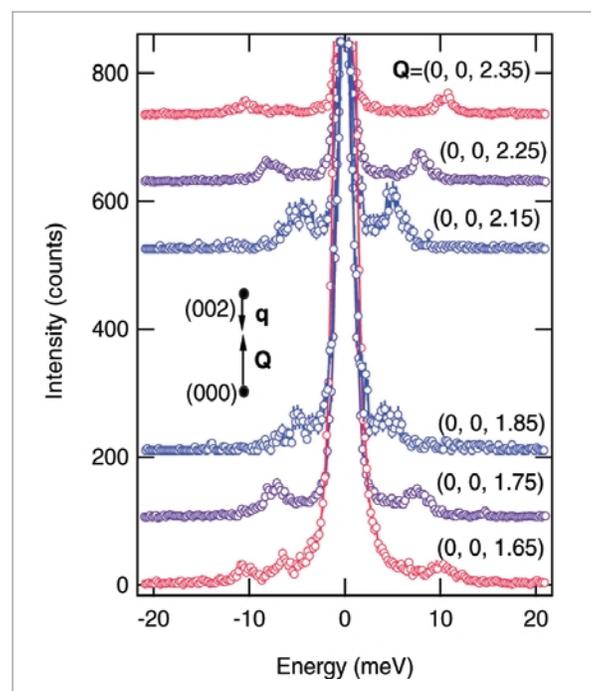


Fig. 1. Raw data, counted 60 seconds per point, showing the dispersion of the $[00c]$ longitudinal-optic phonon mode through the (002) zone center. The scattering vector, Q , is on the c -axis. The phonon wave vector, q , conserves momentum according to $Q = G + q$, where G is a reciprocal lattice vector pointing to the nearest reciprocal lattice point.



Although first known for its unique nuclear properties, uranium also exhibits several unusual solid-state properties that may be studied in terms of quantized lattice vibrations (phonons). Despite the development of inelastic neutron scattering techniques in the 1950s and 1960s, there remains little phonon-dispersion data for many actinides, including uranium. This is because many isotopes have large neutron absorption cross sections, and, even in cases where a suitable isotope exists, crystals large enough for neutron scattering (>0.1 cm³) were rarely grown successfully.

Researchers from the Institute for Transuranium Elements and Los Alamos and Argonne National Laboratories have begun changing this situation by taking advantage of the development of high-resolution inelastic x-ray scattering (IXS) at the APS. Synchrotron-based IXS offers a great opportunity because uranium crystals can be much smaller and, unlike with neutrons, the technique IXS has no special isotope requirements.

In a demonstration experiment, high-purity uranium crystals were grown at Argonne and mounted in a small vacuum chamber at the XOR 3-ID beamline. The researchers obtained phonon-dispersion curves at room temperature with an incident energy of 21.657 keV ($\lambda = 0.57$ Å). This energy was chosen to give a maximum flux at a resolution of ~ 2 meV but was unfortunately just 700 eV above the L_2 edge of uranium at

20.95 keV. Since the crystal thickness of ~ 1 mm was far larger than the penetration depth, all measurements had to be performed in reflection. This requirement represents the most significant disadvantage of IXS for heavy elements in comparison to traditional neutron scattering, since the latter can operate in transmission without the complications involved in thinning crystals.

Nevertheless, the test experiment was a considerable success. Phonon count rates of ~ 1 count/s were obtained from a scattering volume of only $\sim 2 \times 10^{-3}$ mm³, which translates to an equivalent scattering mass of ~ 40 μ g. Modes displacing atoms along [00 ζ] and propagating in all three high-symmetry directions were measured. Whereas the acoustic modes agreed with corresponding neutron-scattering measurements, the longitudinal-optic branch frequencies (Fig. 1) were about 10% higher in energy, yet were consistent with the higher cutoff energies observed in phonon density-of-states measurements involving polycrystals.

REVEALING THE KINETICS OF PHASE TRANSFORMATIONS IN BULK METALLIC GLASS

For the first time, researchers, using the APS, have applied simultaneous diffraction and small-angle x-ray scattering (SAXS) with high-energy x-rays. They used this technique to investigate the kinetics of the amorphous-to-crystalline phase transformation in Zr_{52.5}Cu_{17.9}Ni_{14.6}Al₁₀Ti₅ bulk metallic glass (BMG). Key benefits of this new technique are that (1) it simultaneously probes transformation behavior at two different length scales and (2) the significant penetration power of high-energy x-rays ensures that the measurements are representative of bulk behavior.

Investigating phase transformation kinetics is important because phase transformations are a promising way of making nanostructured materials in large quantities. Potential benefits of increasing the production of nanostructured materials include lower cost and greater market penetration of products that incorporate nanostructured materials. Phase transformations involving nanostructured materials usually occur under conditions far from equilibrium. Although thermodynamics ultimately determines the equilibrium phase for a given set of conditions, whether—and how—the nanostructured phase is produced from the meta-stable precursor depends on kinetic processes.

The *in situ* annealing study was carried out at the XOR 1-ID beamline by using 81-keV x-rays (Fig. 1). Researchers used bulk metallic glass BAM-11, the composition of which was Zr_{52.5}Cu_{17.9}Ni_{14.6}Al₁₀Ti₅. The samples were 1-mm-thick disks with a diameter of 8 mm. The glass and crystallization temperatures, T_g and T_x , were 628K and 714K, as determined from differential scattering calorimetry at a heating rate of 10 K/min. Annealing at 681K–713K leads to 2–10 nm crystalline particles based on x-ray diffraction and transmission electron microscopy studies. Samples were measured in transmission geometry, yielding a probe volume of $0.1 \times 0.1 \times 1$ mm³, and heated by using a furnace constructed at XOR sector 1 at the

This experiment demonstrates the feasibility of a number of experiments, such as uranium phonon dispersion, as a function of temperature and pressure. These experiments are now being planned. ○

See: M.E. Manley¹, G.H. Lander^{1,2}, H. Sinn³, A. Alatas³, W.L. Hults¹, R.J. McQueeney¹, J.L. Smith¹, and J. Willit³, "Phonon dispersion in uranium measured using inelastic x-ray scattering," *Phys. Rev. B* **67**, 052302-052304 (27 February 2003).

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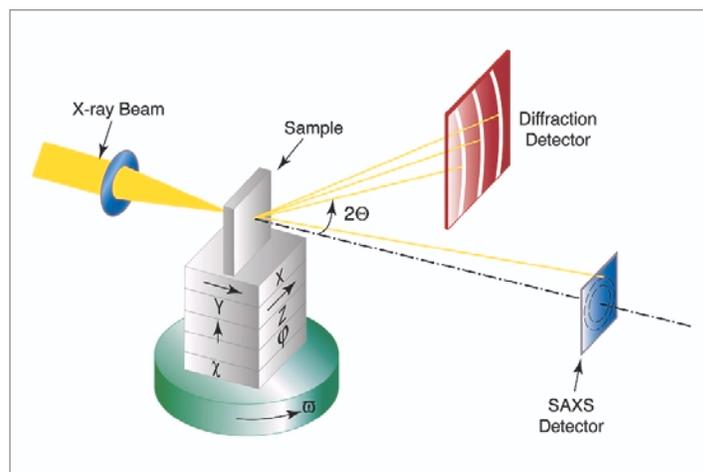


Fig. 1. Schematic diagram of the experiment set-up. Diffraction and small-angle scattering data were recorded simultaneously by using two area detectors. The diffraction detector was mounted on one side to capture a greater range of Q . The samples were 1-mm-thick discs with a diameter of 8 mm. High-energy x-rays (80.7 keV) easily penetrated the sample thickness, ensuring that the measurements were representative of the bulk. Note that the dimensions are not drawn to scale.

APS. Researchers using beamline 1-ID have recently developed a pinhole-based SAXS camera using high-energy x-rays with a Q range of 0.008 – 0.2 \AA^{-1} , where Q is the magnitude of the momentum transfer. To determine the kinetics of both phase separation and crystallization, researchers simultaneously recorded the diffraction and SAXS intensities using two area detectors.

A key finding is that nucleation and growth of the crystalline phase in Zr_{52.5}Cu_{17.9}Ni_{14.6}Al₁₀Ti₅ BMG occur in separate stages, with different kinetics. Phase separation occurred first, setting the stage for crystallization. The crystalline phase obtained by

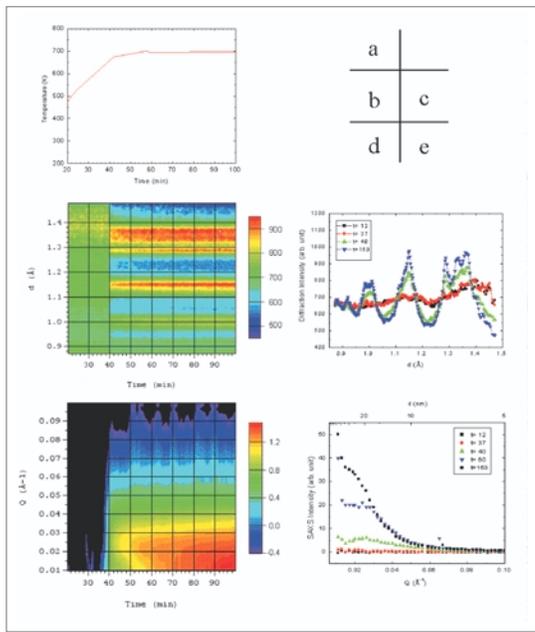


Fig. 2. Simultaneous diffraction and SAXS data obtained with high-energy synchrotron x-rays. (a) Temperature of the sample for $20 < t < 100$ min. (b) Kinetic diffraction diagram for $20 < t < 100$ min. (c) Diffraction patterns at selected annealing times; prominent diffraction peaks appeared at $t = 40$ min. (d) Kinetic diagram of SAXS intensity for $20 < t < 100$ min (in log scale). (e) SAXS profiles at selected annealing times. The top axis gives the corresponding length scale $\left[d = \frac{2\pi}{Q} \right]$ that is being probed.

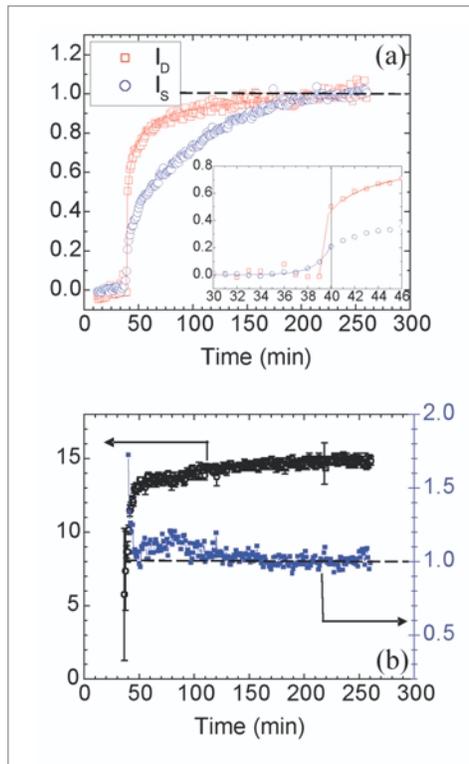


Fig. 3. (a) Integrated diffraction (I_D) and small angle scattering (I_S) intensities as a function of time. (b) Evolution of D_g and $\frac{I_D}{D_g^3}$. D_g is a representative particle size determined from a Guinier analysis of the SAXS data. For a system consisting of uniform-sized particles, $\frac{I_D}{D_g^3} \propto N$, where N is the number of particles. The flat profile seen for $\frac{I_D}{D_g^3}$ indicates that N is held constant during growth. The values of I_D , I_S , and $\frac{I_D}{D_g^3}$ have been normalized to unity (dashed lines) at equilibrium ($t > 200$ min).

annealing at $T \sim 700\text{K}$ is primarily Zr_2Ni , suggesting that Ni and/or Zr atoms are involved in nucleation. How is nucleation of the crystalline phase possible? Researchers believe that the mechanism of nucleation is the homogenous formulation of Ni-rich clusters resulting from the local exchange of atoms. The experimental results support such a mechanism: the first appearance of the SAXS intensity was captured during heating at $T = 630\text{K}$, just above T_g .

Figure 2 shows the simultaneous diffraction and SAXS data. A remarkable feature shown in Fig. 2c is the abrupt change at $t = 40$ min., when prominent diffraction peaks suddenly appeared. Figure 3(b) shows the evolution of D_g , which is a representative particle size determined from a Guinier analysis of SAXS data. The Guinier analysis yields a representative particle size, D_g , of about 15.0 ± 0.3 nm in final equilibrium. By measuring the diffraction and SAXS data simultaneously, the researchers were able to uncover how the BMG material transforms by exploring the kinetics at two different length scales.

The research is not only the first of its kind, but it also has significant implications in terms of applying scattering technology in other ways. For example, researchers found that scattering instruments that can simultaneously measure diffraction and small-angle scattering provide a unique tool for studying phase transformation behaviors and kinetics under non-equilibrium conditions. Also, researchers expect to gain a better understanding of the development of nanostructures as a result of their research. In fact, several instruments under construction at the Spallation Neutron Source have been designed on the basis of anticipated advances in nanostructure technology resulting from these studies.

In summary, APS researchers were able to probe the kinetics of phase transformations at different length scales. The results of the experimental work show that partial crystallization in $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ BMG proceeds in two separate stages—nucleation and growth—with distinctively different kinetics. In addition to providing valuable insight into kinetic mechanisms in this material, the implications of the research are significant in that they may help influence the degree to which nanotechnology will advance in the marketplace. ○

See: X.-L. Wang^{1,2}, J. Almer³, C.T. Liu², Y.D. Wang¹, J.K. Zhao¹, A.D. Stoica¹, D.R. Haeffner³, and W.H. Wang⁴, "In situ Synchrotron Study of Phase Transformation Behaviors in Bulk Metallic Glass by Simultaneous Diffraction and Small Angle Scattering," Phys. Rev. Lett. **91**(26), 265501-1 to 265501-4 (31 December 2003).

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