

RECENT APPLICATIONS OF X RAYS IN CONDENSED MATTER PHYSICS

Advances in x-ray source brightness, detector efficiency, x-ray optics and computing power promise to make the second century of x-ray applications in condensed matter physics as exciting as the first.

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Since their discovery by Wilhelm Conrad Röntgen, x rays have played a significant role in our lives: they make the unseen in our bodies visible; they enhance our security in air travel; they make possible nondestructive testing of a wide variety of materials. And through x-ray diffraction and spectroscopy they make it possible to probe the order of matter at the atomic level.

The discovery of x-ray diffraction in crystals by Max von Laue, Walther Friedrich and Paul Knipping, and William Bragg's subsequent interpretation of the diffraction spots as proof of the wave nature of x rays, laid the foundation for the field of x-ray crystallography. X-ray crystallography proved essential in relating the atomic structure of solids to their functions and physical properties. The intensity distribution in the diffraction pattern was found to reveal how electrons were distributed within the atom and to give information about how the atoms in a solid vibrated about their equilibrium positions. In more complex crystals with unit cells built of molecules, the spot intensities in the regular diffraction pattern were modulated in a way that directly revealed the atomic structure of the molecule—a discovery that revolutionized chemistry and molecular biology. (See the article by Wayne Hendrickson on page 42 of this issue.) Diffraction patterns from the liquid state of matter, while not as detailed as those from the crystalline state, indicated the correlations in the positions of the atoms in the liquid, which formed the basis of the physics of liquids.

Early in the history of x rays, Compton scattering revealed the energy and momentum distributions of electrons as well as vividly illustrating Heisenberg's uncertainty principle. But the real birth of x-ray spectroscopy came with the discovery that Bragg scattering could be used to select x rays of a particular wavelength. Using this technique, Moseley found that the discrete lines superimposed on the continuous bremsstrahlung spectrum varied systematically with the anode material's atomic number, making possible the completion of the periodic

table before all the elements had been chemically separated. X-ray spectroscopy made it possible to determine nondestructively the chemical composition of samples simply by looking at the x-ray fluorescent spectra when the atoms in the sample were excited by x rays or other probes. With a finely focused excitation source, one could determine the chemical composition with very good spatial resolution.

Given the impact x rays had on daily life as well as science during their first 80 years, it is surprising that throughout this time x rays were generated by more or less the same principle Röntgen had discovered, and that x-ray source brightness improved by less than a factor of 100.

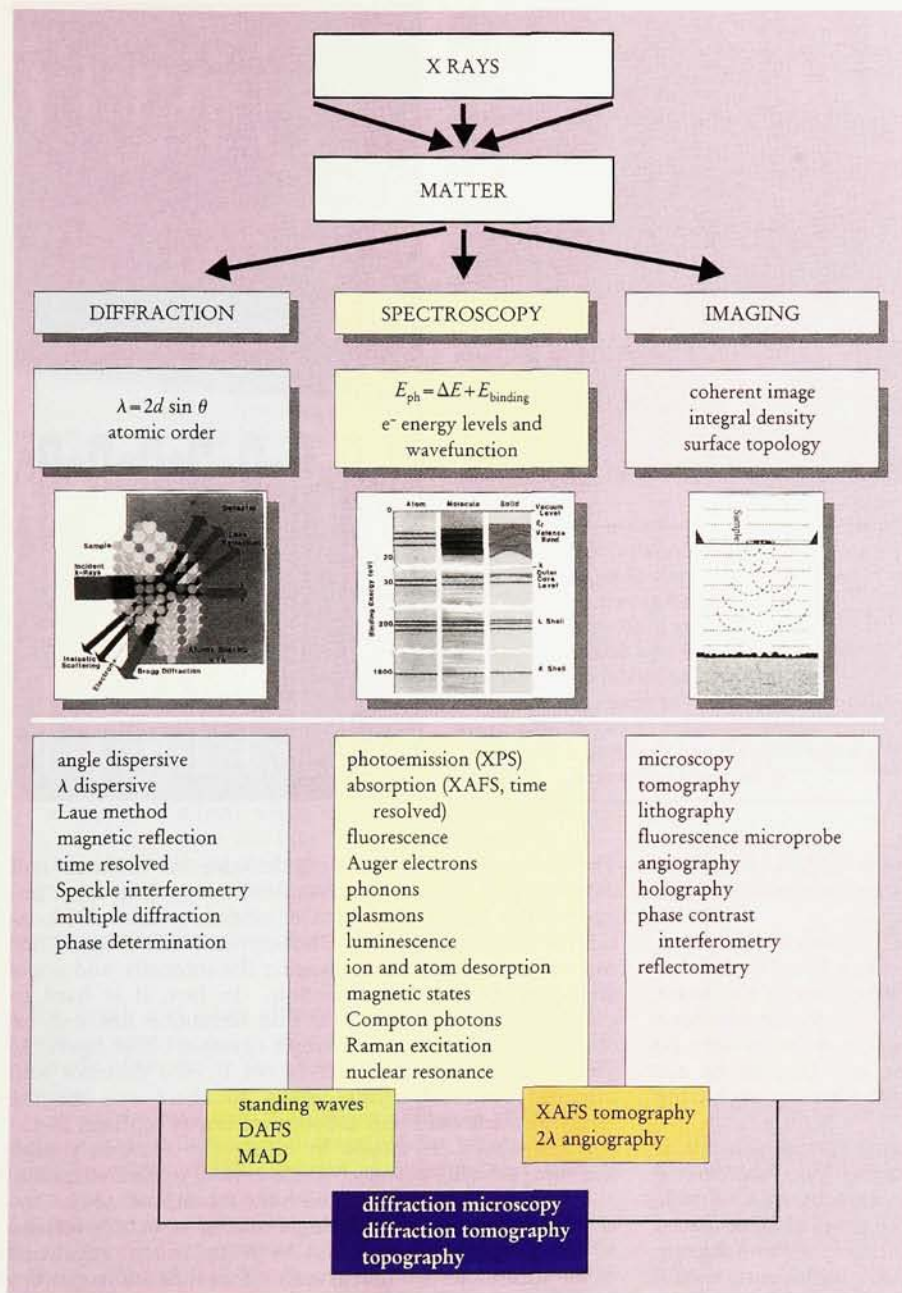
Undulator synchrotron radiation

Particles in a high-energy electron or (positron) accelerator, such as a storage ring, move with a velocity v close to the speed of light, $c \approx 3 \times 10^{10}$ centimeters per second. An undulator imposes an alternating, perpendicular magnetic field on a straight part of the accelerator, forcing the electron beam to oscillate transversely and to emit broadband monochromatic electromagnetic radiation. For simplicity, if the magnetic field has a period of 3 cm, the electron will oscillate at 10^{10} Hz. However, the line-of-sight observer sees the electron oscillations Doppler-shifted by a factor on the order of $[1 - (v/c)]^{-1}$, or of order γ^2 , where γ is the ratio of the electron's energy to its rest mass energy.

For an electron energy of 5 GeV, γ is about 10^4 , and therefore the electron will radiate in the x-ray range at around 10^{18} Hz. Furthermore, because the Doppler effect diminishes rapidly with the angular deviation from the oscillation axis, the x-ray part of the emission spectrum is confined to a cone around the axis with an opening angle on the order of $1/\gamma$, leading to an x-ray beam intensity many orders of magnitude higher than that obtainable from an x-ray tube. Additional benefits include the ability to tune the undulator's fundamental frequency by varying the magnetic field, and the perfect linear polarization and the bunched time structure of the x rays.

Over the last 20 years the brilliance of synchrotron radiation sources has more than doubled every two years! A synchrotron radiation facility with x-ray undulator sources in the 1 to 100 keV region is already operating in Europe; another is under commission in the United States, and one more is under construction in Japan.

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X RAYS IN CONDENSED MATTER PHYSICS. While imaging applications (pink) are probably best known, diffraction (blue) and spectroscopy (yellow) yield equally important information. X-ray diffraction is used primarily to determine the order of matter at the atomic scale. Spectroscopy yields information about the energetics of electrons in different states of matter. Among the most promising new trends are hybrid techniques that combine diffraction with imaging (purple), spectroscopy with diffraction (green) and spectroscopy with imaging (orange). **FIGURE 1**

just its outward form. The low level of diffuse scattering, the small refractive index (less than 10^{-4} smaller than unity) and the strong dependence of absorption on atomic number give rise to high contrast and 1:1 imaging in absorption radiographs. Given sufficient computing power, tomographic recording of the absorption's spatial dependence allows one to reconstruct the structure of matter down to a spatial resolution of about a micron, with this limit currently set by the resolution of available detectors.

When the photon energy increases to the point where core electrons can be excited, abrupt increases in absorption occur. These "absorption edges" are characteristic for each element. By choosing the appropriate energy

Because today's x-ray sources, in which x-ray beams are generated by relativistic electrons or positrons in storage rings (see the box "Undulator synchrotron radiation"), are trillions of times more brilliant, many expect the impact of the second century of x rays to be at least as great as that of the first.

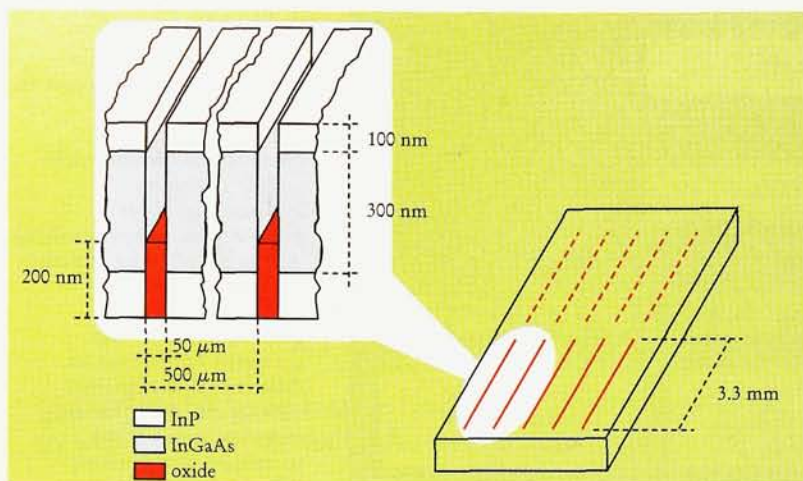
In this article we shall briefly survey some of the current trends in imaging, diffraction and spectroscopy (see figure 1), noting that yet another trend is to combine two or more of these techniques to form new hybrid experiments.

Imaging

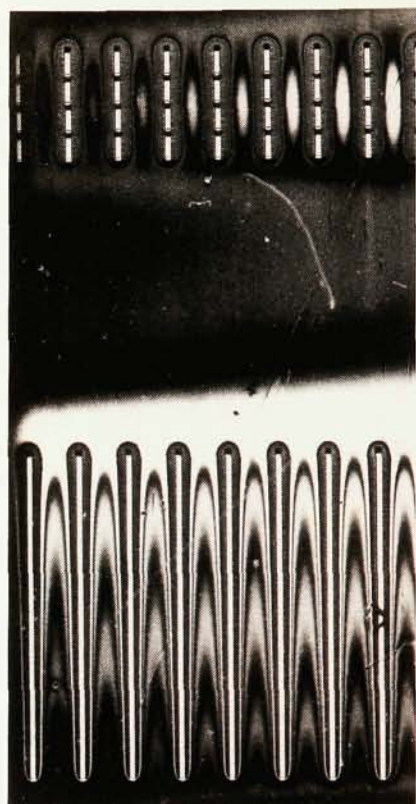
From Röntgen's discovery to the present, imaging has attracted the greatest interest of both the public and specialists in different fields.¹ The penetrating power of x rays reveals the volume properties of matter rather than

from the continuous synchrotron x-ray spectrum, one can obtain element specific tomographs. Present resolution even allows the small energy shift of the edge specific for a particular chemical state of the atom to be mapped out.

Since the minimum distance that can be resolved by a wave of wavelength λ is given by $\alpha\lambda/N_A$, where N_A is the numerical aperture seen from the source/object and α is a factor between 0.5 and 1 determined by the source coherence properties, x rays of Angstrom wavelength should be able to probe structures at the atomic scale. Up till now, however, the best resolution attained with x-ray imaging has been around 100 Å. One reason is that, because the refractive index is so close to unity, conventional optical schemes do not work for x rays. Instead, one uses diffraction lenses such as Fresnel zone plates (FZPs) or curved mirrors at extreme glancing angles where figure errors seriously affect performance.



LAYERED SEMICONDUCTOR STRUCTURE with 300 nanometers of InGaAs and a cap of 100 nm of InP grown on an InP base with oxide ridges is shown schematically (a) and imaged (b) to a depth of about 250 nm by a grazing-incidence synchrotron x-ray beam. The fringe contrast in the x-ray topogram reveals changes in the lattice constant and elemental composition. (Courtesy D. Novikov.) FIGURE 2



In addition, the required beam power is so high that sophisticated methods must be applied to avoid damaging the delicate optical components. Despite these difficulties, several beam focusing schemes have been tested.

Although FZPs are in use at several synchrotron radiation sources with $\lambda > 15 \text{ \AA}$, only recently have attempts to produce transmission FZPs for the conventional x-ray range been reported. So far, Bragg reflection FZPs etched directly into the surface of a silicon crystal have been more successful than transmission FZPs for this range.

Other strategies avoid optical elements altogether. Contact microscopy—with the specimen lying directly on the detector—and projection microscopy—with the beam from a microspot source diverging through the specimen to produce an enlarged picture on the detector—can be used at shorter wavelengths. The detecting media are the resolution-defining elements, with photoresists having a resolution of about 100 \AA .

Another method that avoids using optical elements is x-ray holographic microscopy² employing the Gabor in-line arrangement, in which the incident wave traveling outside the crystal serves as a reference for the phase of the scattered wave. The crucial step is the registration of the hologram and its sequential reconstruction. After initial unsuccessful attempts in the early 1950s to reconstruct and magnify the image with optical light, today's images are stored in photoresists, read out by an atomic force microscope and then numerically reconstructed with a computer. This technique also looks promising for conventional x rays with $\lambda < 10 \text{ \AA}$. Conventional x rays not only will allow study of thicker specimens, but will also enlarge the field of spectromicroscopy to record element and chemical state specific maps for a much larger range of elements. Yet another benefit of harder x rays is the lower level of radiation damage they cause to the specimen.

Spectromicroscopy uses scanning techniques, which require small, focused beam spots. At present, FZPs and mirrors are the favored technique for producing spots down to 200 \AA , but specially designed glass capillaries have successfully generated spots of similar size, and x-ray wave guides are currently being developed.

Bragg diffraction can be used to carry out diffraction microtomography on textured polycrystalline materials.

The strongest impact of x-ray imaging on research and development, however, has resulted from topographic images of the lattice perfection of single crystals. Dislocations, strain patterns and lattice-constant inhomogeneities can easily be detected by imaging the intensity and angle dispersion of a Bragg reflection. In fact, it is hard to overemphasize the influence this technique has had on our ability to grow perfect single crystals. (See figure 2.) The lateral resolution limit is set by the detector and inherent limits of crystal optics to about one micron. Recently, dark field and differential phase contrast methods have been developed by using the extremely high angular resolving power of single-crystal optical elements.

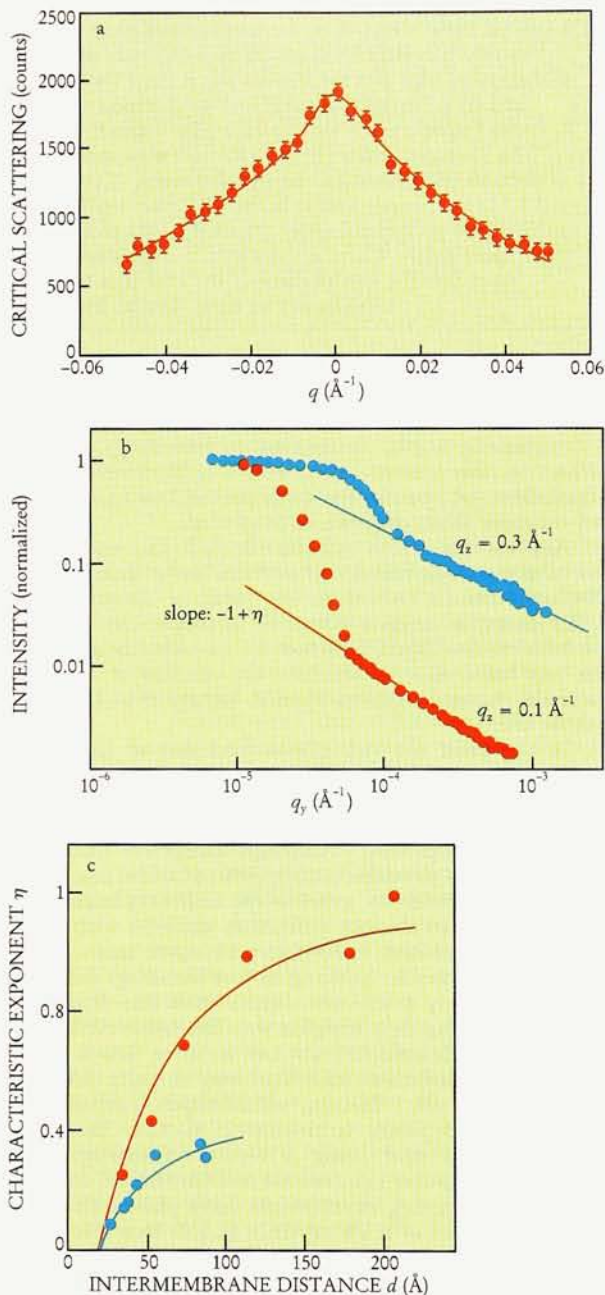
Very recently, researchers have attempted³ to use the scattering pattern from a single unit of structure instead of using signal enhancement by translational repetition of the unit as in crystallography. This diffraction pattern contains geometrical phase information like that in a hologram, but with atomic-scale resolution. Such studies require the full brilliance of modern synchrotron x-radiation sources and the development of detectors with high efficiency, high-count-rate capability and high spatial resolution. If enough computing power is at hand to rapidly analyze the patterns, we can expect great progress in x-ray imaging for several decades to come.

Diffraction

In addition to increasing the resolution attainable in diffraction studies, the increasing brightness of synchrotron radiation sources also makes it possible to study smaller samples. Many crystals can be grown only in minute sizes. Some experiments may require a high degree of crystalline perfection, which as a rule is more easily realizable in a small crystal or by illuminating minute areas of a larger crystal. A tiny amount of matter can be studied under pressures comparable to those deep

ALGEBRAIC DECAY. Many, diverse systems exhibit neither long-range order, in which the pair correlation function of the system's order parameter is constant, nor short-range order, in which the the pair correlation function decays exponentially with r . Rather, the pair correlation function of such systems decays algebraically, as $r^{-1-\eta}$, where η is the characteristic exponent. In x-ray diffraction, long-range order produces sharp Bragg peaks and short-range order produces diffuse, Lorentzian-shaped diffraction peaks. Algebraic decay produces pseudo-Bragg peaks with broad wings, from which η can be determined. **a:** The binary alloy Fe_3Al undergoes a transition from an ordered phase, in which Fe and Al atoms occupy in a perfectly ordered way the corners of a cubic unit cell with an

Fe atom at the center, to a disordered phase, in which the corners are occupied by either Fe or Al with equal probability. For temperatures very near the critical temperature and at shallow depths, the alloy exhibits algebraic decay in agreement with predictions of renormalization group theory (from ref. 6). **b:** The surface of a liquid remains smooth, resisting fluctuations in its height, because of its surface tension. Plotting the intensity of the scattered x rays versus q_y , the component of the x-ray scattering vector parallel to the surface, results in a curve with pseudo-Bragg peaks and broad wings indicative of algebraic decay. η is inversely proportional to the surface tension and proportional to the square of q_z , the perpendicular component of the scattering vector (red and blue curves). (Adapted from ref. 7.) **c:** In a stack of surfactant membranes, the neighbors limit the space available for fluctuations, causing an entropic repulsion, for which η depends on the intermembrane distance d . In a ternary system of oil, water and surfactant, η was measured as a function of d (red), which was varied by changing the oil concentration, and found to agree with the theoretical treatment by Wolfgang Helfrich. If the surfactant's polar head groups are charged, the entropic interaction is overwhelmed and η decreases (blue). (Adapted from ref. 8.) **FIGURE 3**



in the Earth and other planets. Finally, an increasingly important special case of diffraction by a small sample is the study of atoms or molecules confined to a surface or interface.

Shining x rays onto a surface at close to the critical angle of total reflection and detecting the specularly reflected intensity yields a wealth of information.⁴ For a sharp but laterally rough surface, this x-ray reflectivity (XR) measurement gives the correlation in heights across the surface. As an example, consider a single crystal cut so the surface is at a small angle relative to atomic net planes. The resulting surface profile is like a staircase where the steps coincide with the atomic net planes. Recent XR studies of such surfaces in a silicon crystal have shown that the step morphology changes with temperature from a high-temperature, uniform phase with small steps to separated phases of large facets and high steps at low temperatures. This phase separation is analogous to the case of a mixture of two liquids that mix perfectly at high temperatures, but phase-separate at low temperatures.

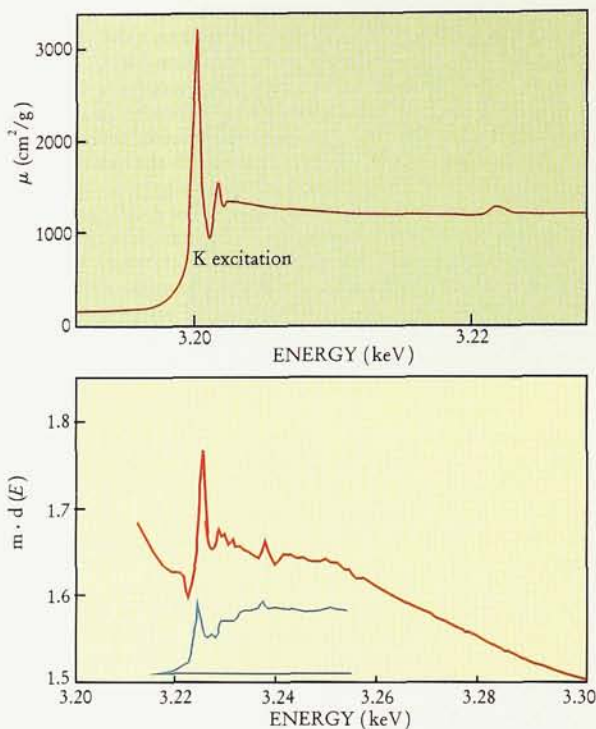
The complementary case to the sharp but rough surface is that for which the density changes gradually in the normal direction across a smooth surface. Here XR determines in a very direct way the average density across the surface. Experiments on simple liquids, such as water and ethanol, showed that the fuzziness of the liquid-vapor interface was fully accounted for by thermally excited capillary waves. In other simple liquids, such as mercury and gallium, as well as liquid crystals in the isotropic

phase, it was discovered that a few well ordered layers form on top of the isotropic liquid.

In heterogeneous systems, such as Langmuir films⁴ (a single molecular layer of amphiphilic molecules deposited on a water substrate), one can accurately measure the thickness of the film and thereby the possible tilt of the molecules with respect to the water surface. Also, one can study how charged polar head groups in the Langmuir film attract ions or how the head groups attract solute molecules, forming nuclei for three-dimensional crystal growth under the film.

X-ray diffraction can also reveal the lateral structure within the interface.⁵ By using an incident x-ray beam at glancing angles near the angle for total external reflection, one creates an evanescent wave with a field whose amplitude decays exponentially perpendicular to the surface. An important feature of this grazing incidence

DRAMATIC IMPROVEMENT in the resolution of x-ray spectral features is evident from comparison of a state-of-the-art K-absorption edge plot for gaseous argon from 1967¹⁰ (top) and an expanded plot made in 1984 (bottom; courtesy R. Frahm) using a much shorter exposure to synchrotron x rays. The dominant feature in the 1967 plot corresponded to a 1s electron being excited to unoccupied states. The feature around 3.222 keV, barely visible in the 1967 plot, results from multielectron excitations, about which the 1984 plot reveals much more detail. Current theoretical calculations¹¹ (blue) reproduce the overall shape of the 1984 plot but vary considerably in many details. FIGURE 4



diffraction (GID) technique is that the probing depth of the evanescent wave can be varied from about a couple of nanometers to tens of nanometers by minute changes of the glancing angle. In contrast to low-energy electron diffraction, the interpretation of the diffraction data is straightforward because the x-ray photon is a weak probe and multiple scattering can be neglected.

Applications of this technique include the reconstruction of many clean metal and semiconductor interfaces in ultrahigh vacuum as well as the study of chemisorption of, for example, oxygen atoms on a copper surface and research on the liquid interface in an electrolyte, where one has been able to see how the surface of a metal electrode changes with an applied voltage over the electrolytic cell.

In the past, the rich phase diagrams of Langmuir layers were studied by classical methods, such as pressure-area isotherms, but modern x-ray diffraction techniques were necessary to determine the nature and interaction of these phases. Although Langmuir films are two-dimensional powders, usually with a lateral grain size of some tens of microns, synchrotron radiation beams are intense enough to produce diffraction patterns with sufficient detail to resolve molecular packing at near-atomic scales. The molecular packing in free-standing, self-supporting films only a few monolayers thick has also been analyzed, yielding new insights into the basic structural features in the transition from two to three dimensions.

Phase transitions at interfaces may be quite different from those in bulk. Melting–solidification, perhaps the most ubiquitous phase transition in nature, has been studied a great deal using a variety of experimental techniques, computer simulations and theoretical calculations. Ion scattering experiments have shown that the top atomic layers of a Pb crystal's (1,1,0) face lose crystalline order tens of degrees below the bulk melting temperature. This astonishing result has been confirmed by GID x-ray diffraction. Surface melting has now been observed in metals, semiconductors, rare gas films, ice and other molecular crystals.

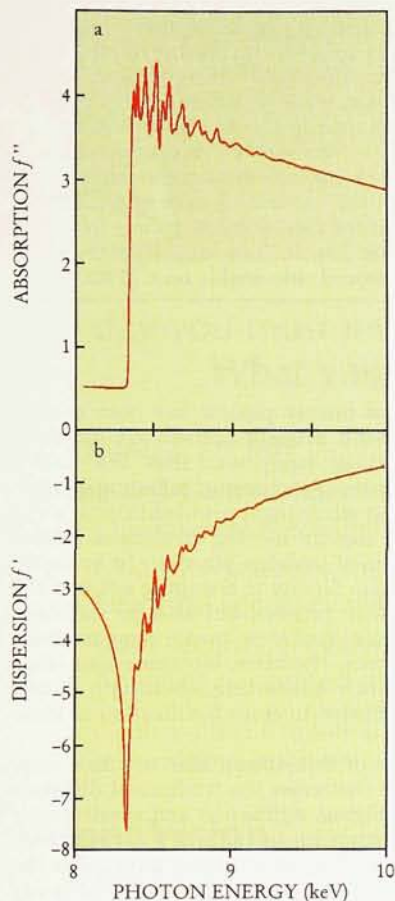
The opposite phenomenon, surface crystallization, also occurs in Nature. One example is the solidification of alkanes—simple hydrocarbon chain molecules terminating in a methyl group at both ends, $\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3$. XR and GID measurements reveal that, at about 3 °C above and persisting down to the bulk solidification temperature, the surface of alkanes forms a single crystalline monolayer. The monolayer has a two-dimensional hexagonal lattice and the molecular axis is perpendicular to the surface.

In melting–solidification, the phenomenon of supercooling is well known, as in, for example, a glaze of frost forming on a road in Winter. Superheating is much less common. One example is the melting of small Pb crystals embedded in an aluminum crystal matrix. Transmission electron microscopy shows that nanometer-sized Pb crystals form close-packed (1,1,1) face octahedra, truncated in

smaller (1,0,0) faces co-aligned with the single crystal Al matrix. As the temperature approaches the melting point from below, x-ray experiments have shown that the (1,0,0) faces become rough while the (1,1,1) faces stay atomically smooth, even at temperatures well above the bulk melting temperature of Pb. Upon melting, the inclusion becomes spherical.

The patterns observed in x-ray diffraction reflect the microscopic structure of different phases of matter in the sample. Crystalline phases produce sharp Bragg diffraction spots, corresponding to long-range order of thousands of angstroms, while liquids give broad diffuse rings indicating short-range order over only a few angstroms. Recent experiments have looked at a state of matter that exhibits neither long-range nor short-range order, but rather the pair correlation function of atomic positions exhibits a peculiar algebraic decay characterized by an exponent, η . In the diffraction pattern, this state gives pseudo-Bragg peaks with broad wings from which the exponent η can be determined. Figure 3 shows data for three such systems, all seemingly quite different. Even studies of two-dimensional “crystalline” order have revealed that such systems actually exhibit algebraic decay.

A particularly advanced application of x-ray diffraction involves the use of x-ray standing wave fields and has become practical only with the availability of sufficiently perfect crystals. In such experiments, one looks not just at the elastically reflected “far-field” intensity far from the crystal, but also at the “near-field” intensity near the surface and inside the dynamically diffracting crystal. Such near-field measurements probe the spatial periodicities of elemental distributions within the bulk and on the surface of the sample. This technique, which is used to measure the positions of foreign atoms inside and on the surfaces of crystals, circumvents the phase problem of kinematical diffraction measurements by using the host lattice as an absolute reference for the position of the pattern.⁹ As one moves the varying electric field of the wave-field nodal planes through the sample, the foreign atom reveals its position by giving off fluorescence



ABSORPTION AND SCATTERING give complementary information about a sample. **a:** The oscillations following the K-absorption edge for crystalline Ni result from backscattering of the photoelectron by neighboring atoms. These oscillations can be analyzed to find the radii and number of atoms occupying neighbor shells as well as more subtle details, such as vibration amplitudes. **b:** In the vicinity of the K-edge resonance, dispersion decreases sharply from its off-resonance value, which is equal to the atomic number of the scattering atom. K-edge frequencies vary for different elements, allowing one to vary the contrast between elements in a sample by varying the photon energy. (Courtesy R. Frahm.) **FIGURE 5**

photons, Auger electrons, photoelectrons or by desorbing. One application of this technique has been *in situ* characterization of the lattice sites of deposited ions on an electrode in an electrolyte as a function of the applied potential and electrolyte conditions. This coupling of x-ray interference and spectroscopy is another excellent example of the exciting possibilities offered by new hybrid methods.

Spectroscopy

Most of what we know about the electrons in different states of matter has been revealed by elastic or inelastic scattering of photons. Prior to the 1950s, x rays played a decisive role in characterizing materials and elucidating atomic structure and the nature of electron-photon interactions. Since the 1950s, new detectors, perfect crystal optics, increased computer power and synchrotron x rays have allowed fundamentally new uses of x-ray spectroscopy.

Figure 4 illustrates the improvement in a state-of-the-art absorption spectrum for argon gas from 1967 to 1984. The additional spectral features in the 1984 spectrum provide information about multielectron interactions in the ground state, the excitation and its subsequent decay. This information can be used to test multielectron relativistic and quantum electrodynamic effects to precisions of better than 10^{-6} of the total binding energy. Such advances are also important for condensed matter physics, because atomic physics forms the basis of condensed matter physics. Figure 5 shows the variation of the real part (associated with scattering amplitude) and the imaginary part (associated with absorption) of the scattering factor of an Ni atom inside a Ni crystal as a function of the

photon energy. Note that because of interactions between the electrons and the crystalline lattice, the oscillating structure above the binding energy extends much further than the oscillating structure for the gas phase in figure 4a. This additional structure gives information about the radius and number of atoms in a neighbor shell.⁹

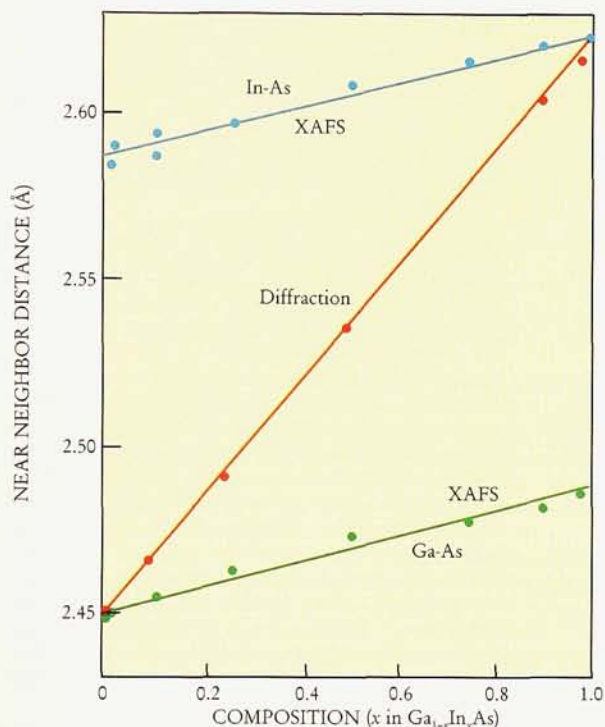
Over the past 20 years, x-ray absorption edge fine structure (XAFS) has proved invaluable in many structural studies. For energies just exceeding the binding energy, the outgoing photoelectron is affected by the spin and angular momentum dependence of the unoccupied states, because selection rules must be satisfied for energy, angular momentum and spin. This gives information about the bonds and exchange interactions between neighbors. At higher energies, the transition matrix element reflects the chemical and geometrical surroundings of the excited atom. Because XAFS does not require long-range crystalline order, it has been used with great success in fields such as catalysis research, often performed *in situ* during reactions. Considerable progress has been made in relating atomic-scale structural features revealed by XAFS spectra to the overall function of the catalyst.

Spectroscopy and diffraction yield complementary information that is necessary for a full understanding of the structure and dynamics of a solid. Information about local structure as revealed by XAFS has also been instrumental in understanding alloys, helping to place in context knowledge of the average structure revealed by diffraction. (See figure 6.) Combining both the diffraction and absorption spectra can reveal, for example, a special symmetry of a noncentrosymmetric crystal, such as $\alpha\text{-Fe}_2\text{O}_3$, that the absorption spectrum alone would miss.

Resonances can also be useful for studying systems that normally interact only weakly with x rays. For example, with respect to charge scattering, magnetic x-ray scattering is suppressed by a factor of $(hv/mc^2)^2$, where v is the x-ray frequency and m the electron rest mass. This suppression, coupled with the relatively small fraction of electrons that contribute to magnetism, means that magnetic interactions are normally too weak to be probed by x rays, unless one uses very hard x rays—an area under active development—or unless one tunes the photon energy to a resonance. The L-edges of rare earth elements and the M-edges of actinides have shown resonance enhancements of several orders of magnitude. As such, one can label magnetic atoms in alloys of such materials and determine the contribution of these atoms. X-ray magnetic scattering provides information that complements that obtained from magnetic neutron scattering, because the selection rules for magnetic x-ray scattering are different from those for magnetic neutron scattering. Thus, for example, the influence of electron spin and momentum on the scattering could be studied separately.

Another outstanding resonance enhancement results from exciting nuclear levels with synchrotron x-ray radiation. Mössbauer photons emitted from stimulated nuclei, such as ^{57}Fe , are available with resolutions ranging from meV to neV with photon intensities on the order of 10^4 per second into a narrow angle.

If the photon energy is very close to an excitation energy, the final state can consist of a hole, a photoelectron and an energy-shifted outgoing photon or of a



LOCAL STRUCTURE REVEALED by x-ray absorption fine-structure spectroscopy complements the average structure information as revealed by diffraction.¹² In a crystal of $Ga_{1-x}In_xAs$, the band structure can be successfully calculated using Vegard's law, which assumes a perfect lattice with an average lattice that varies linearly with x . This dependence is consistent with diffraction measurements of the average nearest-neighbor spacing (red), but is at variance with XAFS data that show that In-As and Ga-As lattice spacings (blue and green, respectively) are close to those for pure InAs and GaAs, respectively, and depend only weakly on x . FIGURE 6

A brighter future

Traditionally, condensed matter physics has been considered "small science," with projects carried out by small groups of scientists using equipment that fits into a standard laboratory space. Synchrotron radiation sources offer such overwhelming advantages over traditional x-ray sources that they are rapidly moving condensed matter physics out of the realm of tabletop physics. In so doing, the synchrotron radiation facility is changing not just the tools of condensed matter physics, but also its sociology. At synchrotron radiation facilities, many comparatively small groups of physicists, chemists, biologists and other researchers are constantly interacting, creating a stimulating atmosphere conducive to cross fertilization of ideas and techniques.

Among the results of this atmosphere are new combined x-ray techniques that cross the traditional divisions of x-ray techniques: imaging, diffraction and spectroscopy. In many ways, the new possibilities offered by synchrotron x-ray sources and the combined techniques have made the present as exciting as the pioneering period of x-ray research at the beginning of the century.

Acknowledgment

Space restrictions for this article have forced us to select only a few dozen of the hundreds of important topics published in this field over the past two decades. Such a selection procedure is always open to criticism. The responsibility for any oversight rests entirely with us. We would like to express our appreciation to the following people for their many helpful and stimulating ideas: B. Batterman, M. Blume, P. Eisenberger, W. Graeff, F. Grey, C. Kunz, L. Leiserowitz, B. Lengeler, A. R. Mackintosh, S. Mochrie, D. Moncton, I. Robinson, W. Schülke, S. K. Sinha, A. Snigirev, B. Sonntag, E. Stern and G. H. Via.

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photoelectron and an Auger electron with two holes. These are Raman transitions, which are well known from the optical regime. The atom passes from the ground state resonantly through virtual intermediate states to this final state. Precise measurements of the energy-shifted photon, the photoelectrons and the Auger electrons not only reveal the nature of this process but also provide details of the involved final and intermediate states. Even inelastic scattering processes connected with additional excitations of valence electrons can be resonantly enhanced. The rotation of the optical plane of the x rays by non-centrosymmetric structures—optical activity—has been measured, as has rotation by an external magnetic field—Faraday rotation.

Spin-polarized XAFS, which provides the possibility of studying the magnetic structure around an atom by using circularly polarized x rays, also appears to be a promising technique for future studies.

Inelastic scattering of off-resonance photons is now used to study plasmons and phonons. Among the exciting recent results is the observation of fast sound in water (3300 meters per second, which is comparable to sound speed in ice) over a large energy-momentum region. For such experiments, one needs highly perfect crystal optical elements to furnish the resolution and a bright source to get enough photons within a bandwidth sufficiently narrow to separate the excitation from noise.

An experiment performed by detecting inelastically scattered photons as the nodes of the standing x-ray wave-field move through regions dominated, respectively, by core and valence electrons demonstrated the existence of plasmon bands and of plasmon band gaps. This indicates that a mean-field approach to calculating the dielectric response of the semiconductor—that is, an approximation assuming a free electron gas oscillating relative to a positive ion core—cannot fully describe the plasmon excitation in covalent crystals, because the periodicity of the positive core potential changes the plasmon collective excitation.