X-ray Diffraction in Two Dimensions

Glancing x-rays at very low angles isolates a surface-specific signal and allows structural studies of two-dimensional physical systems

"Where are the atoms?" This is the fundamental question to be answered before most others when dealing with physical and biological systems at the atomic level. Absence of basic structural information significantly limits, for example, the value of spectroscopic and other types of data. X-ray diffraction has always been the prime means of determining the three-dimensional structure of crystalline materials. But there has never been a generally applicable technique for finding the arrangement of atoms in two-dimensional systems, such as thin films only a few atomic layers deep and the surfaces of solids. Even the surface structure of silicon remains controversial, despite the intensive investigations of this most technologically important material over the years.

Now it seems that x-ray diffraction can be a surface-sensitive tool after all. The newest approach is called grazing-incidence Bragg diffraction. Several experiments have now demonstrated the ability of this technique to do crystallography of solid surfaces, to follow structural changes on surfaces, to investigate thin films of amorphous materials, and to study monolayers of biological macromolecules on solid substrates.

With these successes in mind, researchers are building several new instruments of wide-ranging capability in order to take grazing-incidence Bragg diffraction from the demonstration stage to a state of being able to attack interesting problems. Most future research will likely require the much brighter radiation available only at synchrotron radiation centers.

Synchrotron radiation is, in the eyes of many researchers, the key to using x-rays to study two-dimensional systems. David Moncton of Brookhaven National Laboratory, who has made a career of connecting the two, notes that there are inherently a small number of atoms to scatter the x-rays in surfaces, the interfaces between materials, thin films, membranes, and so on. The brightness of synchrotron radiation compensates for the weak scattering power.

X-rays are such a desirable tool for structural studies because, relatively speaking, they do not interact strongly with the material they are probing. Crystallographers can therefore assume, in interpreting their diffraction patterns, that the only atoms encountered by an x-ray beam are those responsible for the diffraction. X-ray diffraction patterns are therefore directly relatable to the material's structure.

As applied to two-dimensional physical systems, there are some difficulties with x-ray diffraction. One, already mentioned, is that they are only one or a few layers of atoms thick, making the intensities of any diffracted beams weak and difficult to observe in the face of the much stronger diffraction from the substrate supporting the sample. The solution is to somehow eliminate the influence of the substrate. In recent years, two approaches have had great success (*Science*, 20 August 1982, p. 693). One is to work with free-standing films with no substrate. The other is to deposit layers on exfoliated graphite, which is nearly transparent to x-rays and has an extremely high surface to volume ratio.

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Exactly how widely applicable these methods are is still a matter of discussion among researchers, but it is clear that many times it is simply not possible to avoid a thick sample and there may sometimes be reasons for not wanting to. Grazing-incidence Bragg diffraction provides a way to obtain surface information from thick samples. The idea came from Peter Eisenberger of the Exxon Research and Engineering Company. His idea, concocted under the pressure of finding a project for a new postdoctoral associate when he was at Bell Laboratories, was to combine the well-known optical phenomenon of total reflection with Bragg diffraction.

Total reflection occurs when light or any electromagnetic radiation passes from a medium of a higher index of refraction to one of a lower index, provided that the incoming light trajectory makes a very small angle with the plane of the interface between the two media. The critical angle below which total reflection occurs is, from Snell's Law, $\phi = \cos^{-1}(n_{low}/n_{high})$, where n is the index of refraction. For x-rays, the index of refraction of solids and liquids is slightly less than 1, so an x-ray beam in air or vacuum will be totally reflected if its angle of incidence is at or below the critical angle. Grazing-incidence Bragg diffraction therefore has a much enhanced surface sensitivity. The entire x-ray beam is reflected (diffracted) from the surface, enlarging the surface signal. And the x-ray beam does not penetrate into the sample volume, removing the associated large background.

It is important to keep in mind that the grazing angle ϕ is not the Bragg angle θ that occurs in the diffraction equation. Moreover, in a two-dimensional system, the diffracting entities are not planes of atoms but instead are lines of atoms. By rotating the sample about an axis normal to the surface, it is possible to keep a constant grazing angle of incidence but vary the angle the x-ray beam makes with the diffracting lines and thereby generate a diffraction pattern characteristic of the surface geometry.

The first demonstration of these ideas came in 1979, when William Marra, Eisenberger, and Alfred Cho, all of Bell Laboratories, used grazing-incidence Bragg diffraction to examine the interface between a gallium arsenide single crystal and an epitaxially grown aluminum crystalline layer. Since the index of refraction for aluminum is closer to 1 than that of gallium arsenide, it was possible to choose a grazing angle such that total reflection occurred at the interface between the two materials rather than at the aluminum surface. The researchers were able to determine the structural nature of the interface, including a hexagonal distortion that compensates for the 1 percent mismatch between the aluminum and gallium arsenide lattices.

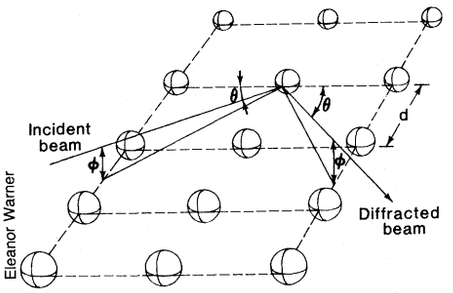
For studying the surfaces of metals and semiconductors, it is necessary to work in an ultrahigh vacuum of 10^{-10} torr or better in order to keep the surface as clean as possible. By 1981, Eisenberger and Marra had completed an ex-

periment with such a vacuum chamber, which they used to study the surface of germanium. In common with many materials, the germanium surface undergoes a reconstruction; that is, the positions of the surface atoms shift with respect to the ideal germanium crystal structure. Reconstruction is driven by the need to lower the surface energy that is generated by the uncompleted bonds of the atoms there. Eisenberger and Marra showed that the atomic displacements in the germanium surface extend at least to the second layer of atoms below the surface and that the amount of displacement supported some proposed theories and excluded others.

Eisenberger and Marra also produced a new wrinkle by showing that it is not necessary to be completely in the total reflection regime for grazing-incidence Bragg reflection to work, if background scattering from the substrate does not interfere. Angles slightly larger than critical are quite satisfactory. They worked at incidence angles of 1° or less, as compared to 0.3° in the earlier study, because more of the x-ray beam intersects the sample at the larger angle.

Paul Fuoss of Bell Laboratories, the postdoc whose work helped stimulate development of the grazing-incidence technique, got into the act in a study of the melting of lead monolayers on copper surfaces that was published last October. Carried out at the Stanford Synchrotron Radiation Laboratory, this was the first experiment to make full use of synchrotron radiation. It was also the grazing-incidence analog of a number of experiments previously carried out by researchers using free-standing liquid crystal films and graphite-supported monolayers of rare gases. Phase transitions in two-dimensional physical systems have been a hot topic in condensed matter physics. The theory is in better shape than it is for three dimensions, so comparison of models and experiments is possible. Moreover, two-dimensional systems have unique behaviors of their own and are not simply scaled-down versions of "real" three-dimensional systems, so they are worth studying apart from any clues they might give to the understanding of the latter. Finally, many instances of two-dimensional systems are of intense interest—biological membranes, to name one.

Lead monolayers on copper have the structure neither of lead nor of copper. The investigators studied lead on a copper (110) surface. Copper has a cubic crystal structure. The (110) refers to a lattice plane that runs diagonally from one edge of the cube to the opposite. In



Surface Bragg diffraction

The incoming x-ray beam makes a grazing angle ϕ with the surface of the sample. It also strikes a line of atoms lying in the surface at an angle θ. Diffraction occurs when θ satisfies the Bragg condition, $n\lambda = 2d \sin\theta$, where n is an integer, λ is the x-ray wavelength, and d is the spacing between the lines of atoms.

agreement with previous studies of another type, Marra, Fuoss, and Eisenberger found that the as-deposited lead atoms are arrayed in a commensurate (5 × 1) structure. Commensurate means that the spacings between the lead atoms are an integer multiple of the spacings between the copper atoms. The (5 × 1) indicates that the integer is 5 in one direction of a rectangular surface unit cell and 1 in the other.

Upon heating the surface to 320°C, the surface melted, as indicated by a shift in the position and shape of the diffraction spots being monitored. Upon cooling, the lead assumed an incommensurate structure, which reappeared after every subsequent melting of the surface. Melting of the incommensurate structure took place at 240°C, well below the bulk lead melting temperature of 327°C, a phenomenon not discovered in the earlier studies.

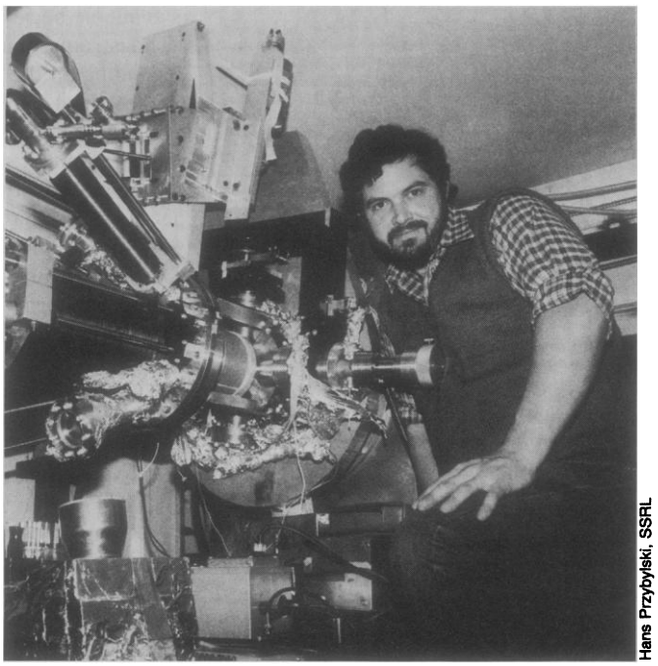
One of the difficulties of surface science is that there is no such thing as an atomically clean surface. Even in the highest vacuum, a surface will quickly be covered by residual hydrocarbon molecules in the vacuum chamber. So surface scientists have to settle for the next best thing, a standard surface prepared in a certain way and characterized by such techniques as Auger electron spectroscopy and low energy electron diffraction (LEED). All of this has to be done in the same vacuum chamber as the experiment in order for the surface to be "accepted." Sean Brennan, who is now at the National Bureau of Standards, built the first of the second generation grazing-incidence Bragg diffractometers that meet this criterion (see photo).

Brennan and Eisenberger continued the investigation of the lead on copper system using x-rays from the Stanford laboratory. They studied the effect of increasing the number of layers of lead from one to about 30. Depth information is available because the x-rays penetrate 25 angstroms or more into the surface, depending on the grazing angle ϕ. In the thickest lead films, they observed three distinct structures. Close to the copper was the commensurate (5 × 1) phase observed previously. Farther from the copper surface, there was an abrupt transition to the incommensurate structure. Farther still, there was a second transition to the normal lead crystal structure. Rather than the (110) orientation of the underlying copper, however, the lead had a (111) surface. The (111) planes of cubic crystals cut diagonally from one corner of the cube to the other.

All of the experiments discussed so far involved monitoring the behavior of only a few spots in the appropriate diffraction pattern. The first successful attempt to reconstruct the structure of a surface from a complete diffraction pattern was reported in April by Ian Robinson of Bell Laboratories. Because gold is a heavy metal and because the x-ray scattering power of elements increases with the square of the atomic number, Robinson was able to obtain data with a 30-kilowatt rotating anode tube.

Robinson also demonstrated a direct way to get vertical as well as in-plane structural information. For a perfect three-dimensional crystal, the diffraction pattern consists of a three-dimensional array of sharp spots. For a perfect two-dimensional crystal, the diffraction pattern is an array of lines perpendicular to the surface. Grazing-incidence Bragg diffraction looks at structure in the plane of the surface and hence sees a two-dimensional array of sharp spots formed by the intersection of a plane parallel to the surface through the array of lines. If there is more than one layer, the lines are no longer uniform, and they contract as the number of layers grows. By measuring the variation in intensity as one scans along the lines, one can obtain the depth information. The simplest way of accomplishing this experimentally is to vary the grazing angle ϕ, but this has the effect of varying the depth below the surface to which the x-rays penetrate and thereby complicates the interpretation of the diffraction pattern. Robinson worked out a way to keep the incident grazing angle constant while varying the exiting grazing angle.

With this technique, Robinson was able to deduce the structure of the top two layers of the (110) surface of gold. Previous experiments of various types had been suggestive but not conclusive and were sometimes contradictory. The surface had a commensurate (2 × 1) structure extending over small regions.



Hans Przybylski, SSRL

The sample sits vertically in an ultrahigh-vacuum chamber having a cylindrical beryllium window through which x-rays enter and exit and which is visible in the center of the photograph. The entire apparatus is about 7 feet long, weighs about 3/4 ton, and is movable. To vary the grazing angle ϕ, rotation is around a vertical axis through the sample. To vary the diffraction angle θ, rotation is around the horizontal axis of the vacuum chamber. In the foreground are devices for cleaning, preparing, and characterizing the surface.

Within these regions, the top layer had a missing row of atoms. The layer beneath was complete but the positions of the atoms were distorted slightly from that of the ideal lattice. Even more surprising was the finding that the top layer spacing was expanded by a large amount (0.6 angstrom). Some surface scientists were at first wary of the finding. However, corroborating evidence has recently come from high-resolution transmission electron microscopy work by L. D. Marks of the Cavendish Laboratory and David J. Smith of the University of Cambridge in the United Kingdom. Electron micrographs of small gold particles showed the same missing row (2×1) structure.

Also fascinating is the finding that separating the strips of (2×1) regions are "domain walls" with a (111) structure. This is consistent with the observations recently reported by a group at the IBM Zürich Laboratory who used the technique of scanning tunneling microscopy (*Science*, 1 April, p. 43).

Grazing-angle Bragg diffraction is by no means limited to purely crystalline materials. X-ray scattering from disordered or amorphous physical or biological systems does not result in sharp diffraction spots because there is no long-range structural order. But short-range order persists, and the scattering patterns contain information about it.

Fuoss of Bell Laboratories and Alice Fischer-Colbrie of Stanford University have recently demonstrated this during a study of the effects of silver on the structure of germanium diselenide. According to the most popular model, this material consists of layers having an amorphous structure. It is of interest as a possible high-resolution photoresist for the delineation of the patterns in microcircuits. Light shining on the surface causes the silver to diffuse into the germanium diselenide, which then undergoes a structural change. In the first round of results with 1500-angstrom-thick films, Fuoss and Fischer-Colbrie clearly saw a sharp diffraction peak corresponding to the spacing between the layers. This peak disappeared as the silver diffused in. Surprisingly, as the thickness of germanium diselenide decreased, the peak remained (provided no silver was present). The expectation was that the orientation of the layers would change to be more parallel with the supporting silicon substrate and therefore would not show up.

One additional feature of the study is that the experiments were carried out in a poor vacuum (roughing vacuum). The point is that ultrahigh-vacuum chambers are not necessary for every two dimensional system one might want to look at. In some cases, a vacuum is definitely not wanted. Consider the investigation of phospholipid monolayers under way at Stanford by Michael Seul and Harden McConnell in collaboration with Eisenberger. Phospholipids are lyotropic liquid crystals. It was therefore important to control the ambient conditions. For the diffraction experiments the monolayers are deposited onto silicon substrates and maintained in a moist helium atmosphere. Diffraction data have demonstrated two-dimensional order in these monolayers. The results also show the applicability of surface diffraction to the investigation of biological molecules largely made up of lighter elements. This encouraged the researchers to think of bigger things.

One of the age-old problems in crystallography of biological molecules is the difficulty of getting them to crystallize. Earlier this year, Egidijus Uzgiris and Roger Kornberg of the Stanford School of Medicine published an account of a method for producing two-dimensional arrays of macromolecules bound to lipid monolayers. Their general method was to deposit the lipid monolayer derivatized with a ligand to which the molecule of interest binds onto an electron microscope grid with the ligands exposed. The grid was then placed in solution containing the molecule to be bound. Transmission electron microscopy was used to examine the resulting arrays.

Seul and McConnell want to use a similar technique to produce arrays to be examined by grazing-incidence x-ray diffraction. McConnell points to several advantages over conventional protein crystallography. Chief among these is the possibility of carrying out structural studies of macromolecules in biologically functional states. McConnell and his co-workers already have indirect evidence for the crystallization of their macromolecules on lipid monolayers.

Perhaps a dozen groups in the United States and Europe are sufficiently impressed with grazing-incidence Bragg diffraction to begin building their own equipment. Keng-san Liang of Exxon, for example, is constructing a grazing-incidence system that will examine adsorbate-covered surfaces under high pressures so that he can study catalytic processes under realistic conditions. Several of the instruments under construction are intended for use at Brookhaven's National Synchrotron Light Source.

The level of activity is all the more impressive considering the investment required to get into the game. Robinson, who is collaborating with Fuoss on one of the new grazing-incidence systems, estimates that a diffractometer together with an ultrahigh-vacuum chamber and electronics will cost $150,000. Auger and LEED equipment for surface characterization add another $20,000 each. And a rotating anode tube is over $120,000. The beam time at a synchrotron radiation facility is free, but there are other expenses associated with working at such a place. However, the need for accurate structural information in two-dimensional systems makes the expense worthwhile.—**ARTHUR L. ROBINSON**