

## X-ray Crystallography of Surfaces and Interfaces

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### Abstract

X-ray crystallographic studies of surface structure have a much shorter history than the IUCr (and crystallography in general) because it is a technique that requires very intense sources of X-rays. It did not become widely practiced until synchrotron-radiation user facilities became established in the 1980s. Since then it has grown steadily to the point that it is now one of the best trusted methods in determining the structures of surfaces and interfaces. This article will emphasize the differences between two- and three-dimensional crystallography and will be illustrated with some examples of important surfaces.

### 1. Introduction

The remarkable success of X-ray crystallography as a means of obtaining high-resolution structural information about molecules can be attributed to the simple fact that the technique averages over a very large ensemble of identical molecules with identical orientations. The method is inherently immune both to defects in the structure itself and to undesirable perturbations of the physical probe, which vary all the way from the Heisenberg uncertainty principle to radiation damage. This happy situation is presented to us by nature through the widespread abundance of crystals, the most common form of solid matter. To appreciate the significance of this truth, one has only to contemplate the state of our knowledge of the structure of liquids, for which crystals do not exist, with that of solids.

When we turn to surfaces and their structures, we are in a situation somewhere between that of solids and liquids. Two-dimensional (2D) crystals cannot exist because an array of identical interacting atoms on a mathematical 2D lattice is inherently unstable to thermal fluctuations. Some 2D assemblies do occur naturally, and have sufficient order for them to be studied with X-ray diffraction, even though they strictly

cannot possess long-range order. More commonplace are structural studies of the 2D state of matter that comes attached to the true crystalline state, namely the *surface* of a true bulk crystal or its *interface* with another medium. Atoms at surfaces have different electrostatic environments and additional restrictions on the number of covalent bonds they can form, so they tend to follow different chemical rules. For this reason, there is no general reason to expect the surface structure to match the lattice spacing presented by the bulk crystal to which it is attached. This will often tend to force the surface to adopt a *reconstruction*. It can, however, merely lead to frustration of incompatible spacings. When this happens, a surface will be inherently disordered or polymorphic in nature. There is no simple way to predict whether a given surface of a bulk crystal will be 'well ordered' or not. A consequence of this is that it is much more common to find the following structural themes than in bulk crystallography:

- (i) partial site occupancy, with randomly placed vacancies;
- (ii) modulated structures, with regularly spaced misfit dislocations;
- (iii) 'mixed' structures, which are a superposition of alternative configurations.

This article will attempt to highlight some of the successes of surface X-ray crystallographic results, but will also emphasize some of the fundamental contrasts between surface and bulk crystallography. For further details, the reader is referred to the reviews by Feidenhans'l (1989) and Robinson & Tweet (1992).

### 2. Notation in surface crystallography

The most general description of the surface of a crystal is an arbitrary boundary at which the crystal ends. Surface crystallography is usually concerned with *low-index* surfaces having orientations given by small-integer Miller indices in the crystal's reciprocal lattice. According to the Miller construction, such surfaces correspond to flat planes which expose relatively close packed 2D arrays of bulk unit cells in real space. This provides a natural coordinate frame in which to describe a surface structure, which applies to the most general case: two of the three defining vectors are taken to be *real-space* lattice vectors, **a** and **b**, of the 2D surface

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array, while the third vector is their mutual perpendicular,  $\mathbf{c}^*$ , which is the original low-index *reciprocal* direction of the chosen surface. The reciprocal-lattice vectors  $\mathbf{a}^*$  and  $\mathbf{b}^*$  are thereby guaranteed to lie in the surface plane also. Because of the inherent 2D property of a surface, it does not matter that this hybrid coordinate frame cannot in general describe the parent three-dimensional crystal lattice; however, most high-symmetry bulk crystals can be so described if a sufficiently large number of layers of bulk unit cells are included in the surface unit cell. Because of the clear differentiation in meaning between the crystallographic *in-plane* and non-crystallographic *out-of-plane* directions, we usually separate from the beginning the *parallel* and *perpendicular* components of the momentum-transfer vector.

The above notation also determines the crystallographic classification of surface structures and the conventional setting of the unit cell. Since they strictly have only 2D periodicity, surface structures are classified by their in-plane *plane group*. When crystallographic theory (or standard software) is employed, the 17 plane groups can be converted into corresponding space groups by capitalizing their symbol and assuming a convenient value for the out-of-plane lattice constant. Conventionally, the in-plane directions are spanned by the Miller indices  $h$  and  $k$  along the  $a^*$  and  $b^*$  reciprocal crystal axes. The out-of-plane direction is taken to be the  $c$  axis, which is always the same direction as  $\mathbf{c}^*$ , and the perpendicular component of the momentum-transfer vector is denoted by the index  $L$ , which is now a continuous variable. Use of the capital  $L$  both avoids the typographic ambiguity with the character '1' and reminds the user of its special definition. This convention corresponds to the standard setting of all 17 respective allowed space groups.

Operationally, it is necessary to revise a few other definitions for surface crystallography. Details are given in Robinson (1990), and are summarized here. Firstly, the definition of a structure factor is no longer an absolute quantity measured in electrons. The diffraction from a 2D object is a continuous function of  $L$ , so it must be defined as a structure-factor *density* in units of electrons per unit (reciprocal) length of rod. In practice, the interval of reciprocal length is determined by a slit setting of the diffractometer, and so the measured structure-factor density depends on the instrumental resolution. Secondly, the natural choice for intensity measurements is the 'extended-face' geometry (Warren, 1969) in which a sample (of centimetre dimensions) is much larger than the millimetre-sized beam. Either a very small entrance slit is required or, if grazing incidence angles are used, the beam is caused to spill off the sides of the sample. In this latter case, an area correction to the integrated intensity (Robinson, 1990) is employed for normalization. With multiple-axis diffractometers, such as the five-circle and six-circle configurations, this

area correction can become a rather complicated function of the setting (Vlieg, 1997).

Finally, it is necessary during measurements to keep track of incidence and exit angles,  $\alpha_i$  and  $\alpha_f$ , of the beam with respect to the surface. This is used to correct for *refraction* when  $\alpha_i$  or  $\alpha_f$  becomes close to the critical angle for total external reflection,  $\alpha_C$ , and also to control the allowed range of  $L$  for which both  $\alpha_i$  and  $\alpha_f$  are positive, since usually no diffraction will be detected in transmission through a massive bulk sample on which only the surface is being measured. Refraction affects both the beam directions, hence the value of momentum transfer, and also the intensity which results. A formalism called the distorted-wave Born approximation was introduced to account for this by Vineyard (1982).

### 3. Principal distinctions between bulk and surface crystallography

New diffraction constructs emerge from consideration of the situation of the surface as a perturbation of the bulk. Of these, the most important concept is the crystal truncation rod (CTR) introduced by Robinson (1986). The simplest situation to consider is a crystal terminated by an ideal plane. The diffraction pattern is rigorously expressed as a Fourier transform of the electron density, which now ends abruptly at the surface. The Fourier transform of this density step is a  $1/q$  function which modifies the amplitude of every Bragg peak in the crystal's diffraction pattern through the convolution theorem. The result is to add a  $1/\Delta q^2$  intensity tail to each bulk peak along the direction of the surface normal, which, in our hybrid coordinate frame, is the direction spanned by the index  $L$ . Since the  $L$  direction is a bulk reciprocal-lattice direction, the bulk Bragg peaks will be aligned in linear arrays and these tails join them together to form continuous ridges of diffraction extending all the way through reciprocal space, as illustrated in Fig. 1. Note that the construction of the CTR is based entirely on kinematical diffraction concepts, yet it explains the tails of Bragg peaks in the 'Bragg' diffraction geometry, previously thought to be a consequence of the dynamical theory (Pinsker, 1978). Structural modifications such as relaxation of layer spacings in the vicinity of the surface, expected on theoretical grounds, lead to changes of the intensity distribution along the CTRs. Surface roughness, manifested as a more diffuse termination of the crystal, also modifies the CTR in a characteristic way. The roughness and its characterization are important new aspects that must be added to the meaning of the 'structure' of a surface, analogous to the interpretation of the Debye-Waller factor in traditional crystallography. The effects of both relaxation and roughness on the CTR are shown in Fig. 1.

A second new construct is that of the X-ray specular reflectivity profile. This can be simply thought of as a

small-angle version of the CTR, the  $1/q^2$  intensity tail about the origin of reciprocal space. The conventional reflectivity measurement geometry, leading to Fresnel's law of reflection, uses a different normalization of the intensity which gives a  $1/q^4$  intensity profile for a perfectly flat surface. The sensitivity to surface structure was derived by Als-Nielsen (1987), in the kinematic approximation, by integration of the Fourier transform by parts to obtain a 'master formula'. The dependence of specular reflectivity on perpendicular momentum transfer is similar to the CTR illustrated in Fig. 1. Once again, roughness leads to a general loss of reflectivity, which can be readily measured. The lost intensity reappears as a general diffuse scattering, called the *off-specular reflectivity*, which has been analyzed by Sinha *et al.* (1988). Simple assumptions are made to describe the lateral correlation properties of the roughness in terms of a length exponent,  $\alpha$ , which leads to a closed-form expression for the entire off-specular reflectivity function.

Turning now to results, it is worthwhile to summarize some of the important principles of surface structure learned from X-ray crystallography. We find in general that the observed structures can be classified by different degrees of broken symmetry, starting with the broken translation symmetry of the bulk crystal where it

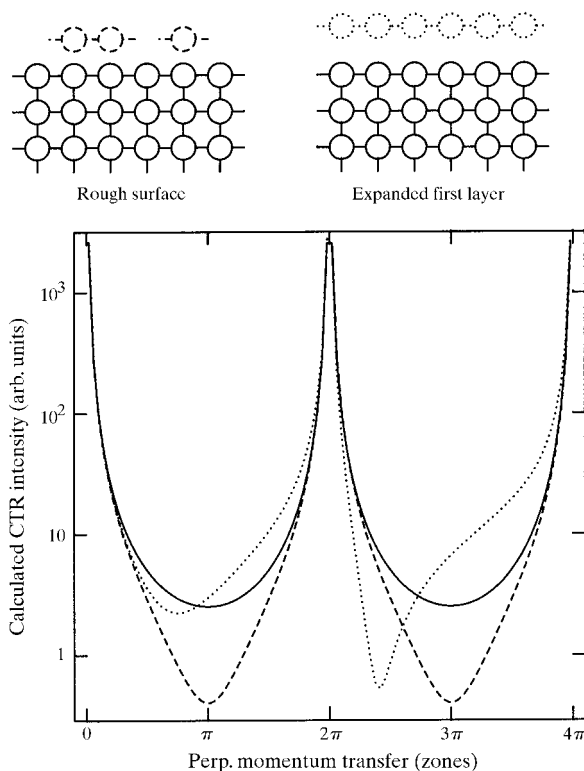


Fig. 1. The intensity of a crystal truncation rod (CTR) calculated as a function of perpendicular momentum transfer,  $L$ , for a simple structure ending abruptly. Also shown are the curves for a rough surface and one showing relaxation of a single layer of atoms.

is cut off by the surface. The simplest broken symmetry is called *relaxation*, which gives rise to a change in the intensities of CTRs alone and no additional diffraction. Relaxed surfaces have been extensively studied by low-energy electron diffraction (LEED), which, being a backscattering technique, is extremely sensitive to changes of layer spacing. For metal surfaces, the empirical rule established by Jona *et al.* (1982) is that the outermost layer spacing contracts to immerse the ionic cores of the metal atoms in greater free-electron density. The resulting charge transfer leads to a net repulsion in lower layers and the result is an *oscillatory* variation of layer spacing with depth in the metal, as is observed. Theoretically, this effect has been explained by Smoluchowski (1941) as a real-space Friedel oscillation due to the reciprocal-space cut-off of the electron distribution by the Fermi level.

A more dramatic rearrangement of the surface structure that breaks the translational symmetry parallel to the surface is *reconstruction*. Generally speaking, when atomic neighbors are removed by the termination of a crystal, the atoms left behind will regroup in a way that alters their bond lengths and angles. This can be described in chemical terms by the loss of a coordination shell or by the introduction of 'dangling' covalent bonds where the neighbors used to be. The new arrangement will often have shorter bonds or new bond angles, which leads to a mismatch with the rest of the crystal. This either results in strain, as in the *relaxation* mechanism discussed above, or else an altogether different structure with a new periodicity in-plane. The most impressive example of this is the (111) surface of Si, which was shown by Takayanagi *et al.* (1985) to have the dimer-adatom stacking-fault (DAS) structure shown in Fig. 2. Takayanagi solved the structure by crystallographic analysis of 2D transmission electron diffraction data, which are analogous to 2D X-ray structure factors. The mismatch of the surface with the bulk Si structure, seen in Fig. 2, leads to a lateral periodicity seven times greater in both directions. Consequently, additional diffraction features occur, called *superstructure rods*, which are also continuous functions of perpendicular momentum transfer,  $L$ . The nomenclature introduced by Wood (1964) labels Si(111) as a ' $7 \times 7R0^\circ$ ' structure denoting the multiplication factors between surface and bulk lattices along the  $a$  and  $b$  in-plane directions and the rotation angle between the two lattices. Subsequent X-ray crystallographic refinement of the Si(111) $7 \times 7$  structure by Robinson *et al.* (1988) found a pattern of lateral displacements increasing from the centers to the outsides of the two triangular islands in the structure, supporting the idea that strain builds up in the structure until it is relieved by the dimer rows along the edges of the unit cell, which act as surface dislocations.

Another principle of surface structures is the existence of a strain field extending far into the bulk of the crystal. This is generally explained by the elastic

response of the crystal to the perturbation of the atomic rearrangement on its surface. Crystallography is the principal way to measure this strain field at the microscopic level. These aspects are invisible to purely surface sensitive methods such as scanning tunneling microscopy (STM), which literally just scratches the surface. The strain field is just one example of a physical property of the solid that is graded with depth near to a surface. More generally, the degree of order near to surfaces will respond to the break of symmetry in a variety of ways, all of which can be probed by surface X-ray diffraction methods. Surface melting, studied by Denier van der Gon *et al.* (1991), is the presence of a thin film of liquid in equilibrium with the solid at a temperature very close to the melting point. Conversely, layering has been seen at the surface of liquid metals such as Hg and Ga in reflectivity experiments by Regan *et al.* (1995). Anisotropic chemical ordering has been seen in  $\text{Cu}_3\text{Au}(001)$  surfaces at temperatures well above

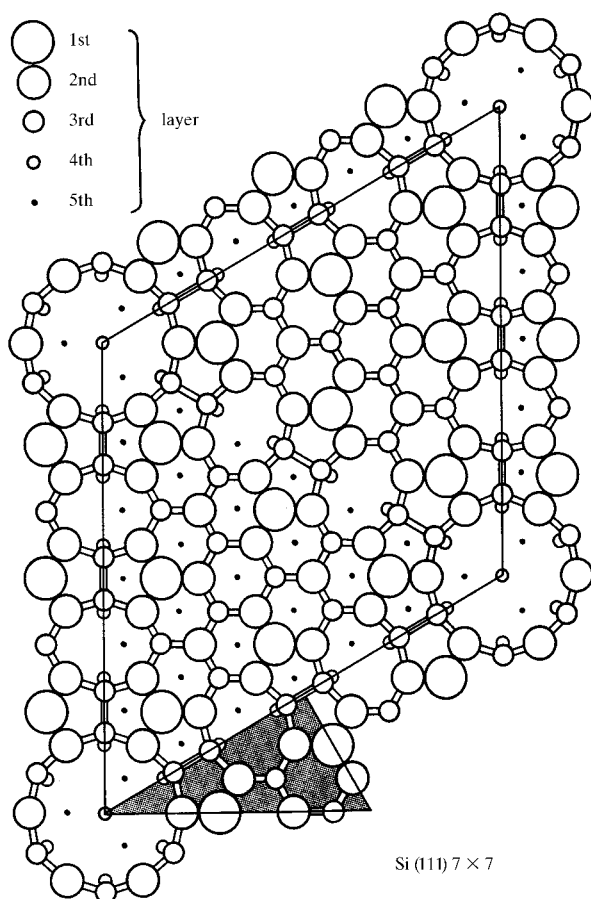


Fig. 2.  $\text{Si}(111)7 \times 7$  reconstructed surface structure, as determined by Takayanagi *et al.* (1985). The three main features in the unit cell are: (i) the triangular islands, one of which has a stacking fault between it and the bulk, (ii) the dimer rows, which are the dislocations connecting the faulted and unfaulted islands, and (iii) the 'adatoms' decorating the outer surface.

the bulk disordering temperature by Reichert *et al.* (1995) and by Robinson & Eng (1995). The data in Fig. 3 show that the surface chemical ordering of the CTR is ten times more intense than that of the bulk. The peak is sharp in the in-plane direction because the short-range-order domains are maintained in register with each other across the surface.

An important new application of X-ray crystallography is to study the interface formed between a surface and some medium, such as a gas or liquid which might undergo some chemical reaction at the interface. By far the biggest area of application of surface X-ray crystallography is the study of adsorbed monolayers on 2D crystalline substrates, usually themselves surfaces of other materials. If the surface is a metal and the medium is  $\text{H}_2\text{O}$ , we have the important case of an electrochemical interface. The example shown in Fig. 4 is of an ordered monolayer of  $\text{CuSO}_4$  structure formed on an  $\text{Au}(111)$  electrode, which forms a  $\sqrt{3} \times \sqrt{3}R30^\circ$  superstructure. The sulfate ions are attached above vacant holes in the plane of the Cu atoms in order to maintain reasonable bond lengths. Here the crystallographic measurements were made by Toney *et al.* (1995) *in situ* with the  $\text{H}_2\text{SO}_4$  electrolyte held in place by a thin plastic membrane. Maintaining potential control was essential in this experiment because the structure transforms from this one with  $2/3$  monolayer of Cu into one with a full monolayer coverage of Cu at slightly lower potential.

Crystallographic information about surfaces can also be obtained by exploiting dynamical diffraction effects. When an X-ray beam enters or leaves a crystal with a grazing angle,  $\alpha_i$  or  $\alpha_f$ , comparable with the critical angle for total external reflection,  $\alpha_c$ , an evanescent wave travelling parallel to the surface is generated. The penetration of this wave into the crystal can be accurately controlled and a 'scattering depth' defined to account for the effects of both  $\alpha_i$  and  $\alpha_f$ . Dosch (1992) has shown how depth-sensitive crystallographic measurements can be made. Another important application of dynamical effects is the X-ray standing-wave method invented by Batterman (1964) and widely employed for structural analysis of adsorbed monolayers.

#### 4. Future outlook for surface crystallography

It is rewarding to look ahead to the many things already possible in traditional bulk crystallography that can be extended to surfaces in the future. Many, but not all, of the current limitations of surface X-ray crystallography can be attributed to the available sources of X-rays. In these, there have been orders-of-magnitude improvements in the last few years, and some of their potential has yet to be reached. Some of the limitations are more fundamental: one obvious future direction is just to construct more complex surfaces. However, as mentioned above, some surfaces are inherently disor-

dered or polymorphic and this will become a bigger problem when attempts are made to assemble ever more complicated molecules into monolayers. Eventually the radiation damage limit will also be reached.

One aspect of structure that does not require dramatic improvements in technique is the study of anharmonicity. Anharmonicity is expected to be significantly more important for an atom at a surface for the simple reason that it has no neighbors on one side. The methods for describing anisotropic Debye–Waller factors with anharmonicity have been established by Johnson & Levy (1974). The main requirement is of crystallographic data with high resolution and accuracy. Crystallographic data collection for surfaces has improved steadily over the years, from  $R$  factors (on intensity) worse than 15%, often limited by counting statistics, to typical values below 5% today. This situa-

tion may improve further when more attention is paid to beam and beamline stability problems.

An example of anharmonicity induced by a monolayer of K adsorbed on Ag(001) is shown in Fig. 5, as measured by Meyerheim *et al.* (1997). The picture is a contour map of the probability of finding the Ag atoms in the outermost two layers of the crystal, viewed from the side. The second-layer Ag<sub>(2)</sub> has a normal symmetric shape, while the outermost Ag<sub>(1)</sub> is asymmetrically extended towards the vacuum side. This map has been generated following a structure refinement using anharmonic vibration parameters for Ag<sub>(1)</sub>. This yielded a large negative value for the third-order  $C^{333}$  coefficient, corresponding to the strongly asymmetric vibrational motion indicated in Fig. 5.

Another area of future exploration using the new synchrotron-radiation sources is the study of surfaces or monolayers of *light elements*, previously inaccessible because their diffraction intensity is relatively weak. A major area of application for the study of surfaces is the understanding of the functioning principles of industrial catalysts, which largely concern small organic molecules. For example, molecular CO adsorption on Ni was

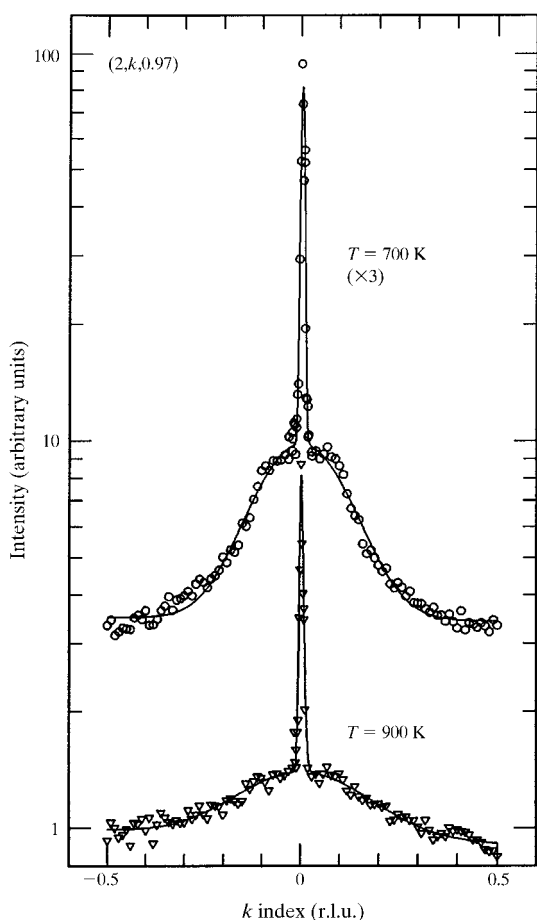


Fig. 3. Short-range order (SRO) in  $\text{Cu}_3\text{Au}$  seen through a reciprocal-lattice scan passing through the 201 superstructure reflection at two temperatures, both above  $T_{\text{disorder}}$ . The broad peak is the conventional SRO scattering peak, while the narrow one is the CTR arising from the (001) surface of the sample. The profile of the CTR is also peaked at 201 due to the laterally aligned SRO domains at the surface.

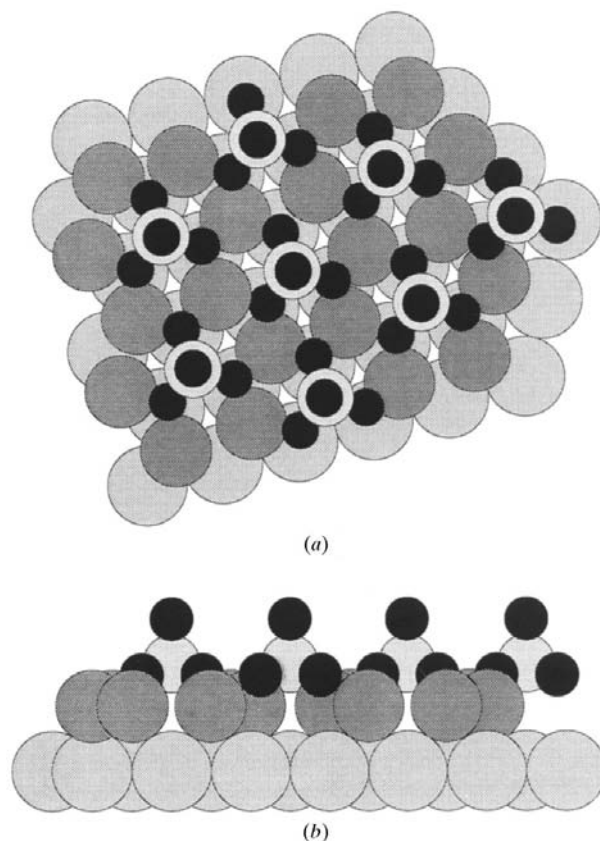


Fig. 4. Copper sulfate monolayer on Au(111) from Toney *et al.* (1995). Top and side views are shown. Large and small light-grey atoms are Au and S, dark-grey atoms are Cu and dark atoms are O.

recently investigated at the European Synchrotron Radiation Facility by Robinson *et al.* (1995). Diamond surface reconstructions have also been investigated by Huisman *et al.* (1997). In the future, it may become possible to see positions of H atoms, which are highly relevant to catalysis mechanisms. It is expected that electron density in bonding electrons will become accessible also. The study of surface phonons, already known from He scattering experiments to display lower-frequency modes than are allowed in the bulk, may benefit from the emerging technique of inelastic X-ray diffraction.

The existence of surface magnetism has for a long time attracted theoretical interest and has recently been detected in two cases using magnetic X-ray diffraction. CTRs extending from antiferromagnetically allowed diffraction peaks in  $\text{UO}_2$  have been observed by Watson *et al.* (1997). The data shown in Fig. 6 are magnetic asymmetry ratios (MAR) measured along CTRs by Ferrer *et al.* (1997) for a sample of  $\text{Co}_3\text{Pt}(111)$ . The MAR is the normalized change of diffracted intensity obtained by reversing a magnetic field applied to the sample. Bulk Bragg peaks of  $\text{Co}_3\text{Pt}$  have a MAR that is attributed to a magnetic moment of  $-0.9$  Bohr magnetons induced on the non-magnetic Pt atoms by the neighboring magnetic Co. The theoretical curve passing through the data of Fig. 6 was obtained by assuming an enhanced Pt concentration of 0.60 in the surface layer with each Pt having a reduced moment of  $-0.43$  Bohr magnetons. The enrichment of the surface layer is understood to arise from the lower surface energy of Pt than Co, *i.e.* segregation. Since the moment on Pt is induced by the magnetic Co, it is reasonable that this is suppressed at the surface because Pt is more concentrated there.

Until now there have been no successful general automatic methods for *solving* surface crystallographic structures, although there are some promising begin-

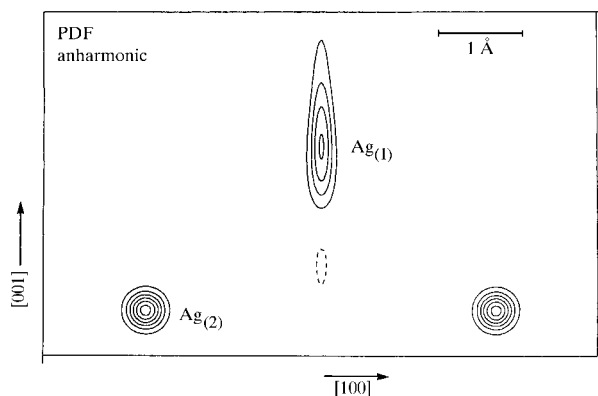


Fig. 5. Probability density map of the outer two layers of an  $\text{Ag}(100)$  surface made to reconstruct by the addition of K. The  $[100]$  and  $[001]$  directions indicated are parallel and perpendicular to the surface.

nings for both traditional direct methods and maximum entropy, such as the works of Carvalho *et al.* (1996) or Collazo-Davila *et al.* (1998). Most structures solved to date have used Patterson, difference-Fourier or guess-and-refine methods. In devising a direct method, the critical question may be the handling of the CTRs, since these contain both surface and bulk information mixed together. The bulk structure is usually known and therefore should be a useful source of initial phase information. Simply omitting the CTRs from the data, as mainly tried to date, is probably too big a limitation. Recently, Moritz & Vogler (1998) have proposed a new maximum-entropy method that *starts* with the CTRs and the known bulk structure, then adds the superstructure reflections later.

The field of surface X-ray crystallography owes much to the following individuals, with whom I have had the pleasure of working and discussing the ideas as they have evolved: Jens Als-Nielsen, Peter Bennett, Bob Birgeneau, Sean Brennan, Jakob Bohr, Fabio Comin, Ed Conrad, Kevin D'Amico, Helmut Dosch, Victor Etgens, Peter Eng, Ken Evans-Lutterodt, Ken Liang, Simon Mochrie, Dave Moncton, Robert Feidenhans'l, Roberto Felici, Salvador Ferrer, Paul Fuoss, Doon Gibbs,

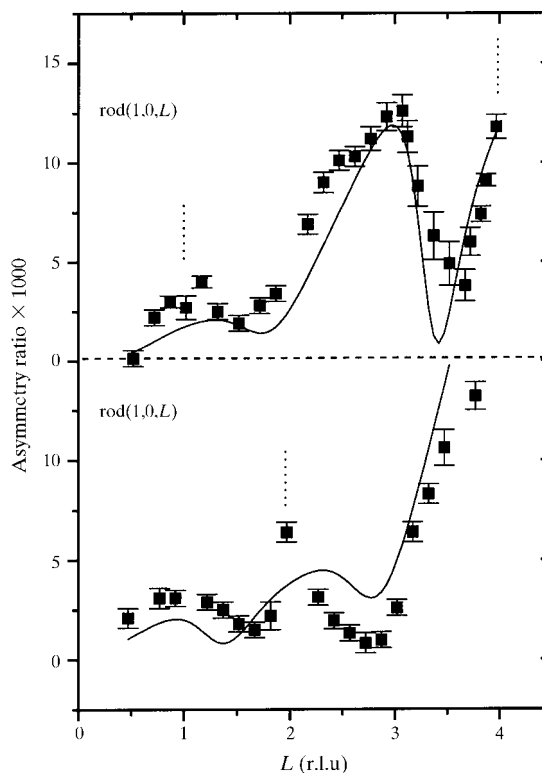


Fig. 6. Magnetic asymmetry ratios (MAR) measured by Ferrer *et al.* (1997) for a sample of  $\text{Co}_3\text{Pt}(111)$ . Two different CTRs are shown together with a theoretical fit curve.

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