X-RAY DIFFRACTION APPLIED TO THE STUDY OF DEFECTS IN SURFACES

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ABSTRACT

The role of x-ray diffraction in characterising defects in crystals is reviewed briefly. It is most sensitive to the presence of plane defects which destroy the long-range order. The same argument is shown to apply to line defects in surface structures. Two recent glancing incidence x-ray diffraction experiments provide contrasting examples: randomly distributed steps are found in the Au(110) reconstructed surface, while regular arrays of domain walls modify certain phases of krypton monolayers physisorbed on graphite substrates.

X-ray diffraction is a long-range structural probe. By averaging a large volume of crystal, it is able to filter out the local imperfections and see only the regularly repeating unit. The Fourier components of the atomic arrangement are the structure factor amplitudes measured at the discrete points of reciprocal space where diffraction occurs in a perfect crystal.

It is only when there are a sufficient number of some regular kind of defect that any change from the perfect diffraction behaviour of a crystal can be detected. The reciprocal property of Fourier transforms means that point defects give rise to scattering that is diffuse in all three dimensions, line defects give planes of diffuse scattering, and plane defects give diffuse lines of scattering. Because the scattering is the most confined in reciprocal space, plane defects are the easiest of the three to detect, and we will limit the discussion to this case, although it can be generalized. Since the presence of randomly distributed plane defects interrupts the coherence of the crystal lattice, it leads to a diffraction broadening in the direction normal to the defect plane. The amount of broadening is inversely related to the spatial extent of the coherent regions between the defects, thus to the defect density. The *shape* of the diffraction peaks is therefore related to the *distribution* of the defects by a Fourier transform. The hardest information to obtain is the actual atomic arrangement within the defect, but this may sometimes be inferred from the relative amounts of broadening of different diffraction peaks, and in special cases from the pattern of displacements of the peaks from their rational positions in the reciprocal lattice. Such a

Mat. Res. Soc. Symp. Proc. Vol. 41. © 1985 Materials Research Society

special case is found here in the Au(110) surface.

A different situation arises when the defects are uniformly spaced throughout the sample. This happens when the mutual repulsion between the defects is stronger than the pinning force so causes them to be equally spaced. This forms an incommensurate structure with a new periodicity, so its diffraction peaks are displaced from the rational (commensurate) positions, but are sharp instead of broad for the random defect case. Physisorbed krypton layers on graphite demonstrate this behaviour.

When we consider diffraction from surfaces, we must reduce the dimension of the whole argument by one. The plane defect becomes a line defect, which separates coherently scattering areas on the surface. The diffraction, already diffuse in the direction normal to the surface, becomes broadened in the (in-plane) direction perpendicular to the randomly distributed line defects as well. The analysis of the line shapes in terms of defect distributions and the pattern of displacements in terms of atomic arrangements are exactly analogous. The kinds of surface line defect we encounter in this paper are surface steps modifying reconstructed surfaces and domain walls in the choice of registry of physisorbed gases on graphite.

Since it was appreciated around 1978 that x-ray sources had evolved to the point that diffraction experiments with single monolayers of atoms on crystal surfaces were possible, there have been a number of results published [1]. With 'conventional' rotating anode sources the experiments are right at the limit of feasibility, and it is necessary to choose heavy elements in small unit cells as the experimental system. With the advent of routinely-available sources of synchrotron radiation, we expect rapid growth of the number of successful experiments of a much more general kind. Many research groups are planning and assembling the necessary instruments [2].

It is a straightforward application of the Thomson electron scattering formula to calculate that the cross section for a single monolayer of atoms can be as high as 10^{-7} for x-ray wavelengths around 1Å [1]. Conventional sources can produce 10^8 photons per second and synchrotron sources 10^{11} per second, but only at a cost of having a beam that is well-collimated in one direction and poorly so in the other. To match this asymmetric resolution function to the diffraction pattern of the surface to be measured, we must use the "glancing incidence" geometry in which the incident and diffracted x-ray beams make small angles to the surface [1]. Experiments can be done in transmission through a thin sample: the same in-plane information is sampled, but with a loss of a factor of 10 to 100 in signal rate. Both experiments reported here benefitted from the use of glancing incidence.

Defects in the Au(110) reconstructed surface

This surface of gold reconstructs by a doubling of the unit cell in the manner of figure 1. This "missing row" structure has been independently derived from previously published x-ray diffraction work [3] as well as low energy electron diffraction (LEED) analysis [4], electron tunnelling microscope images [5] and high-resolution transmission electron microscope pictures [6]. The model in figure 1 exemplifies two distinct types of surface reconstruction: "density modification" or "topological" reconstruction in which bonds between surface atoms are broken and atoms move to an altogether different part of the surface, and "weak" or "displacive" reconstruction where the surface symmetry is spontaneously lowered by Jahn-Teller-like distortions (in this case, in the second layer). Though it is now generally agreed that the morphology is correct, some of the quantitative aspects of the model are still in question. Discussing these focusses on the differences between the techniques involved.

Surface x-ray diffraction, in the form described above, and LEED are complementary techniques in the sense that they sample different subsets of reciprocal space: x-ray data usually correspond to momentum transfer vectors lying close to the surface plane, whereas LEED analyses are usually based on a small number of beams close to the backscattering position. There are no fundamental reasons why more complete data could not be obtained in either case. Nevertheless, in their customary forms, both techniques give information both parallel and perpendicular to the surface; however, LEED is more accurate in the normal direction while x-ray diffraction favours the in-plane information, as the error-bars in figure 1 indicate. The LEED analysis of Au(110) [4] failed to detect the in-plane displacement which is the dominant feature of the x-ray data; subsequent LEED calculations using a greater number of beams support the finding

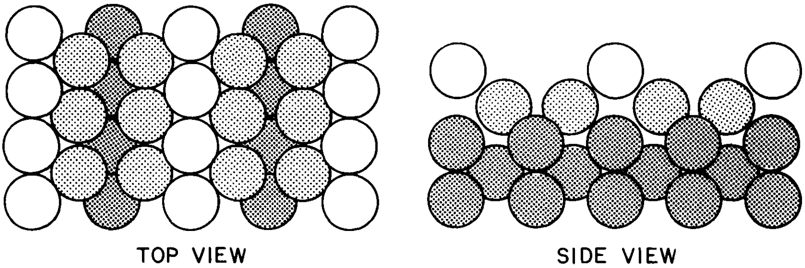

Figure 1. Missing row model of the (110) surface of gold. Two layers are reconstructed: the top layer (unshaded) with 50% occupancy and the second layer (light shading) with lateral displacements of 0.012±0.002Å. Three layers of bulk (heavy shading) are also shown. The top layer spacing is shown to be enlarged by 0.6±0.4Å based on previous x-ray diffraction results [3].

[W. Moritz, private communication]. Excellent quantitative agreement also comes from Rutherford backscattering measurements [7].

The question of vertical displacements of the top layer is much more open: x-ray diffraction shows an *outward* displacement of 0.6±0.4Å [3]; LEED shows an *inward* motion of 0.22Å [4], transmission electron microscopy sees 0.36±0.07Å *outward* [6], and Rutherford backscattering finds a displacement greater than 0.25Å but cannot determine its sign [7]. Theoretical approaches to the problem have been no more revealing: tight-binding band structure calculations showed an outward relaxation of 0.06Å [8]; Monte Carlo simulations gave an inward shift of 0.10Å [9]. There is clearly inconsistency here which remains to be resolved. One possibility is that there is a significant buckling of the third layer: this would affect the x-ray diffraction profiles perpendicular to the surface in a similar way to the top layer expansion. Further investigation requires more complete x-ray data than are presently available.

Fortunately, the analysis of the *defect* structure and the detailed *atomic* structure of a surface are orthogonal problems: atomic structure is contained in structure factors integrated over a diffraction peak, while defect information comes from the careful analysis of lineshapes. Figure 2 shows that different preparations of the Au(110) surface can have different profiles, hence defect arrangements; the same behaviour is seen for each diffraction peak, so it is only necessary to consider one of them. The figure also shows fits to the data which are calculated from the model described below.

The lineshapes have two characteristics: they are *broad* in the [100] direction along the surface but sharp (resolution-limited) in the orthogonal [011] in-plane direction (they are, of course, very broad in the $[01\bar{1}]$ direction perpendicular to the surface); unusually however, the peaks are also *displaced* along [100] in a systematic pattern of alternating direction. The displacements can be large: the peak in figure 2(b) is displaced more than 10% of the distance to the next Bragg peak. The uniaxial broadening implies disorder in one direction only, hence must be associated with line defects oriented perpendicular to that [100] direction. Recalling that line defects in a two-dimensional system are analogous to plane defects in three dimensions, we turn to the theory of diffraction from bulk systems with stacking fault disorder [10]. Broadening to a functional form,

$$F(q) = \{1 - \alpha e^{iqa} - (1-\alpha)e^{2iqa}\}^{-1}$$

$$|F|^2 = \{4\sin^2(\frac{qa}{2})\,(1 + (1-\alpha)^2 + 2(1-\alpha)\cos qa)\}^{-1} \qquad (1)$$

is appropriate to systems with randomly distributed stacking faults in simple lattices. F(q) is the scattering amplitude as a function of momentum transfer q, α is the fault density and a is the lattice constant. Equation (1) explains the line broadening in figure 2, but not the peak displacements.

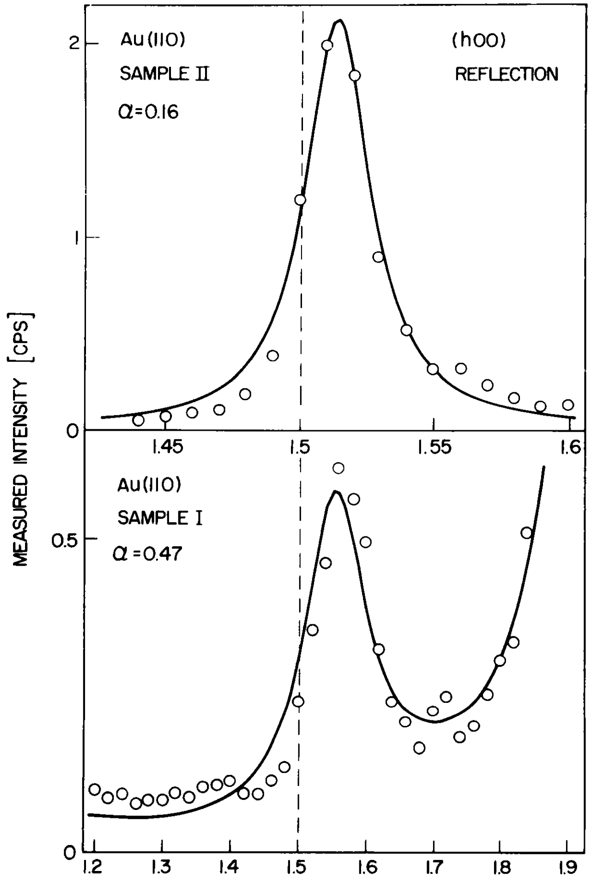

Figure 2. Diffraction intensity as a function of miller index h along the [h00] reciprocal space direction. Parts (a) and (b), for different preparations of the Au(110) surface, have different displacements of the (3/2, 0, 0) peak. The curves superimposed are fits of equation (2) with the values of defect density, α, shown.

A bulk system that shows both uniaxial line broadening and the same pattern of peak displacements (but with the opposite sign) is magnesium fluorogermanate [11]. This has a four-layer structure in which a common form of defect is a missing layer, as seen in lattice images of the crystal. The diffraction pattern is broad and displaced in the faulting direction, in an equal and opposite sense to the observations for Au(110). The same effect is seen in certain protein-DNA cocrystals, where it is also attributed to a missing layer in the stacking sequence [S. Harrison, private communication]. Figure 3 shows magnesium fluorogermanate with its missing 'C' layers, and also a related structure with extra 'A' layers inserted that would have the diffraction peaks shifted in the opposite direction. The structure factor of magnesium fluorogermanate is modulated by the function,

$$F(a) = \{1 - \alpha e^{3iqa} - (1-\alpha)e^{4iqa}\}^{-1} ,$$

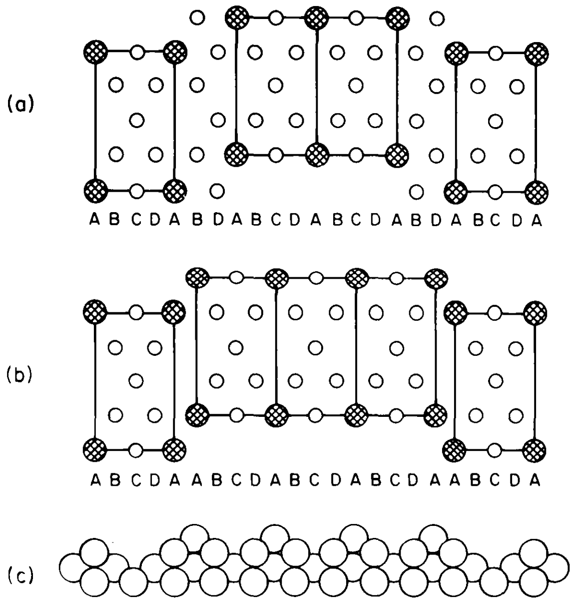

Figure 3(a). Structure of magnesium fluorogermanate due to Cowley [11]. Germanium (shaded) and magnesium atoms in the x = 0 plane of the unit cell are shown. The structure has a four-layer repeat along c and stacking-faults are formed by the deletion of the C-layer. (b) Hypothetical stacking-fault structure formed by insertion of extra A-layers into magnesium fluorogermanate. This would have its odd-l diffraction peaks shifted in the opposite direction. (c) Side view of the Au(110) surface with monoatomic steps corresponding to the stacking faults of (b). The diffraction pattern has the same pattern of shifted peaks.

while that of the hypothetical structure is modulated by [1]

$$F(q) = \{1 - \alpha e^{iqa} - (1-\alpha)e^{4iqa}\}^{-1} . \tag{2}$$

These functions have the characteristic shapes of the diffraction peaks.

We see in figure 2 that eq. (2) describes the Au(110) lineshape very well. Least squares fits are superimposed on the data. Two adjustable parameters were used, defect density α and a scale factor. A component representing the thermal diffuse background was also added in the lower case, because the peak was spread out over such a large range of q. The slight systematic deviation of the curve from the data is due to an asymmetry in the latter, which can be explained by a slight mutual repulsion of the stacking faults (defects): instead of there being a completely random distribution, there is a slightly lower probability of finding two defects close together.

Having established the analogy between the observed diffraction behaviour for this surface and that of stacking-fault defects in bulk systems, we can now ask what is the structure of the line defect. First, we must consider the possibility that the surface reflects a stacking-fault structure inside the bulk; this is ruled out by the observation that peak displacements change readily with surface preparation conditions. We suggest the model of figure 3(c), drawn on a suitable scale for comparison with fig. 3(b). The line defects are monoatomic steps in the surface, which give rise to the same phase relationships between the domains of pure structure.

We note that this kind of defect is a prominent feature of tunnelling microscope images of Au(110) [5]. These images are also consistent with the x-ray observation of long coherence lengths (sharp peaks) in the surface [011] direction. The other defects seen to interrupt the regular 2×1 missing-row regions in these images are double missing rows (3×1 repeat) and triple missing rows (4×1 repeat). We are insensitive to the presence of the latter as they do not change the periodicity, but we can say that the density of 3×1 repeating units is much less than the density of the monoatomic steps: 3×1 defects would lead to surface antiphase domains, hence broadened but unshifted peaks, with functional form (1).

The presence of steps in the Au(110) surface had also been inferred from LEED lineshape studies [12]. The authors discuss whether the broadening of half-order LEED spots is due to steps or to 1×1 units (absent 'missing rows' in the surface); they conclude the former. A distribution of 1×1 units, like 3×1 units mentioned above, gives surface antiphase domains and the lineshape of eq. (1). LEED has difficulty distinguishing shifted peaks (eq. (2)) from just broadened ones (eq. (1)) because of its poor absolute accuracy and distortions in the electron optics. X-ray diffraction, seeing shifted peaks, can immediately rule out the presence of a dominant contribution of 1×1 units to the diffraction.

The density of defects seen in our most disordered sample, $\alpha = 0.47$ is comparable to that published in tunnelling microscope images [5]. Other preparations of Au(110) have had $\alpha = 0.16$ and $\alpha = 0.07$. The defect density appears to be inversely correlated with the annealing time of the sample: a sample annealed for a very long time (many days) would have an almost perfect 2×1 reconstruction with no defects. This assumes that steps are both up and down and so can annihilate each other; there is an *intrinsic* step density of $\alpha = 0.005$ in our samples due to the imperfect cut of the material used, which must be a practical lower limit.

Domain Walls in Physisorbed Krypton Monolayers

Our second example is a two component system: monolayer Kr adsorbed on graphite (Gr) [13]. This is a system in which the "defects" involved are caused by the iteraction of the Kr-Kr and Kr-Gr potentials. The behavior of these defects can be controlled by varying the substrate temperature and/or the vapor pressure of the Kr gas. The substrate was a natural single crystal which was cleaned *in situ* by resistive heating to ≈600° C. The sample cell was filled with Kr at low temperature while the diffraction signature of the two-dimensional Kr solid was monitored with x-rays at the Stanford Synchrotron Radiation Laboratory (SSRL) in the glancing incidence geometry.

The phase diagram near one monolayer for the Kr/Gr system is fairly well-understood [14]. The experiments reported here were done at a pressure of ≈ 2 torr and temperature at or below 95K in a cell which was large enough that the system remained at nearly constant pressure at all temperatures. The first condensed phase observed as the sample was cooled was the $\sqrt{3} \times \sqrt{3}$ solid which defined one monlayer of coverage and had one Kr atom per three Gr hexagons. This had very sharp diffraction features which were used to determine the surface quality of the substrate: the surface was seen to possess coherent regions which were ≈ 10000Å in size. This was despite the multidomain structure of the substrate which exists for the natural crystals. Below 90.5K the solid underwent a *melting* transition from the commensurate $\sqrt{3} \times \sqrt{3}$ structure to a denser incommensurate "fluid" phase which has been discussed previously in detail [14]. As temperature was lowered further, this fluid condensed into an incommensurate solid.

The "defects" which occur in this incommensurate solid are the domain walls (misfit dislocations) of the structure. This weakly incommensurate solid is able to accommodate more Kr atoms than the commensurate solid by breaking up into regions of commensurate solid separated by a regular hexagonal array of domain walls in which the Kr atoms shift from one $\sqrt{3} \times \sqrt{3}$ sub-lattice to another. Though these defects were seen to be regularly spaced, as evidenced by the sharp diffraction lineshape and the presence of a satellite diffraction peak on the low-q side of the commensurate position, their separation was temperature-dependent. Decreasing temperature caused the commensurate domain size to shrink, and brought the walls closer together. The defects are thus a manifestation of the system's efforts to balance competition between Kr-Kr and Kr-Gr potentials. These regularly spaced domain walls are a distinct contrast to the randomly distributed ones in the Au(110) surface: the first has sharp, displaced diffraction peaks with satellites; the second has broad, displaced peaks extending all the way to the commensurate position.

As temperature is lowered the domain wall separation becomes progressively smaller until the overlayer must rotate to *misalign* itself with the substrate in order to offset the increasing strain energy due to the defect concentration. This overlayer rotation was first predicted by Novaco and McTague [15]. The continuous transition to a misaligned structure was found to occur as a function of the misfit between the incommensurate Kr lattice constant and the lattice constant of the $\sqrt{3} \times \sqrt{3}$ structure. This dependence of rotation angle upon misfit is illustrated in Fig. 4. This shows both the prediction of the Novaco-McTague theory which neglects the

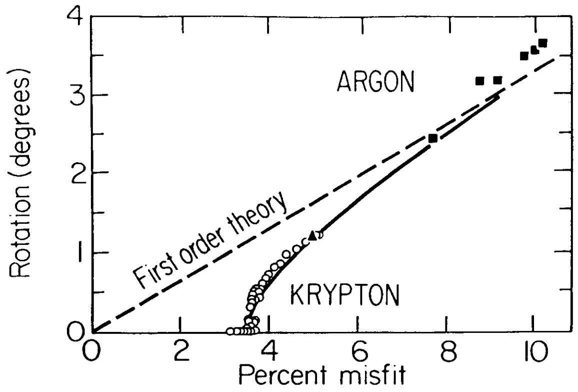

Figure 4. Rotation angle as a function of misfit for Kr (circles, ref. 13 and triangle, ref. 17) and Ar (ref. 18). Ar data are best understood by Novaco-McTague first order theory which neglects influence of defects (dashed line) whereas Kr data are correctly described by Shiba theory (solid curve) which includes defects.

influence of the hexagonal domain walls (dashed curve), as well as the prediction of a theory due to Shiba [16] which does include their influence (solid curve). It is clear that the role of the defects is important, since the rotation is not observed to begin until a finite critical misfit is reached (here ≈3.5%), as the Shiba theory requires: the defect concentration takes on a well defined value before the system chooses the misaligned orientation. This concentration is presumably a sensitive function of the interplay between Kr-Kr and Kr-Gr potentials and should vary from one adsorbate to another.

In summary, we have shown that an x-ray measurement can be used to determine the behavior of defects in an adsorbate system. By controlling their concentration, one can determine the manner in which the system's stability is influenced by them.

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