

Structure Factor Determination in Surface X-ray Diffraction*

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Abstract

A set of formulae is derived for correcting integrated diffraction intensities for surface structure analysis. These differ significantly from their bulk counterparts because of the diffuse nature of the peaks. In-plane and out-of-plane data collection are treated separately. Measurements of $W(001)$ surface diffraction are used as a case study.

1. Introduction

In recent years there has been much progress in the application of X-ray diffraction techniques to surfaces and interfaces. The first experimental study of a clean surface in vacuum was by Eisenberger and Marra (1981), and there have been a dozen examples since. The basic reason for the development of the technique was that X-ray diffraction is highly kinematical (in this case) and intensity measurements could be directly interpreted by means of Fourier transformation and other linear methods. This opened two important avenues of research: crystallography of surfaces to determine structures, and lineshape analysis to study ordering and phase transitions. Both of these are fundamental in surface science, and in both cases the interpretation of X-ray results is more straightforward than for competing techniques. Because the cross section of a monolayer is so small, most work has been done with synchrotron radiation. However, this is not an absolute requirement and, indeed, all the results presented here were obtained with a rotating anode source.

We are of course assuming implicitly that it is possible to make accurate measurements of X-ray diffraction intensities in the first place. This is certainly true in conventional crystallography, as witnessed by its success in the determination of atomic structure and bonding. This paper will consider the special problems of extending the methods of bulk crystallography to the surface case. No emphasis will be placed on sample preparation and its reproducibility, although these are certainly important problems (Robinson 1987). The central theme will be structure factor determination although many of the results are important in lineshape analysis as well.

Surfaces and interfaces may be considered initially to be ideal two-dimensional (2D) objects, consisting of a perfectly flat monolayer of atoms. Real surfaces sometimes

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come close to this ideal, but more often involve a certain amount of out-of-plane structure, either in the form of vertical displacement or in the form of multilayer structures involving a small number of layers. A good example is the W(001) surface which we discuss throughout this paper. The ideal surface obtained by cutting the bulk tungsten crystal is shown in Fig. 1*a*. This state happens to be unstable and the surface *reconstructs* at low temperature by lowering its symmetry thereby gaining stability. The accepted model before our work, due to Debe and King (1977), based on low energy electron diffraction (LEED) results, is shown in Fig. 1*b*. The reconstruction involves lateral displacements of a single layer. The surface unit cell (box) is double the area of the bulk and contains two atoms.

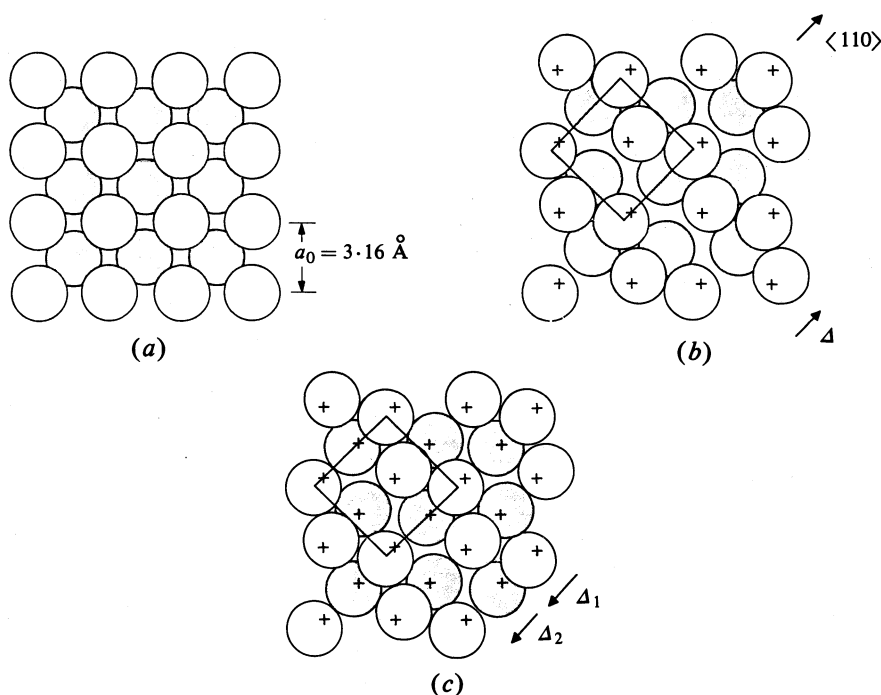


Fig. 1. Top views of the atomic positions in the W(001) surface: (a) without reconstruction; (b) in the model of Debe and King (1977), with pairwise displacements of top layer atoms; and (c) in the model of Altman *et al.* (1988) (see Section 4), where second layer displacements are added.

The diffraction pattern of a 2D object, such as the surface structure of Fig. 1*b*, is an array of diffraction 'rods' which are sharp in the two directions parallel to the crystal surface and diffuse in the perpendicular direction. If the structure is an ideal monolayer, the intensity profiles of the rods will be featureless, continuous functions of perpendicular momentum transfer showing only the effects of the atom form factor and Debye-Waller (DW) factor. If the structure contains more than one reconstructed layer, or vertical displacements, the 3D effects will be apparent in the form of modulation of the rod profile intensity. The crystallographic 'data' that are

then required are the set of rod profiles $I_{hk}(l)$, where h and k are discrete and l is a continuous variable. These replace the traditional I_{hkl} .

For the reconstructed W(001) surface in Fig. 1*b*, h and k take *half-integer* values because the surface periodicity is doubled. This readily allows measurement of the surface in the presence of the bulk crystal because the latter contributes only thermal diffuse scattering (TDS) at the fractional order positions. There are, of course, equally important contributions of the surface at integer h, k positions, which can also be measured provided l is not also an integer (bulk Bragg condition). Here, however, the interpretation is more complicated because of the contributions of crystal truncation rods (CTR) from the bulk: the abrupt truncation of the crystal broadens the bulk Bragg peaks along the perpendicular line. The $I_{hk}(l)$ profiles for h, k integer are measured in the same way, but their interpretation requires understanding surface and bulk effects simultaneously (Robinson 1986).

Historically, surface X-ray crystallographic work has used only fractional order $I_{hk}(l)$ data. Integer order data have been used to determine registry information between a reconstructed layer and its bulk (Feidenhans'l *et al.* 1987) or as a consistency check (Robinson *et al.* 1988), but these data are customarily ignored because of the problem of isolating the CTR and surface structure components. Another simplification has also been made in the majority of experimental studies: structure factors have usually been measured at or near $l = 0$ only and the out-of-plane information ignored. The I_{hk} numbers are treated as 2D structure factors, yielding upon analysis a *projection* of the surface structure onto the plane. The measurement of $l = 0$ structure factors is relatively well understood; however, difficulties in making accurate out-of-plane measurements is one of the main reasons that this kind of data has not been more widely used. This paper first reviews the considerations applicable to the accuracy of $l = 0$ data, then develops the necessary generalisation for $I_{hk}(l)$. This is illustrated with recent new results for W(001) (Altman *et al.* 1988), which depend entirely on the accuracy of out-of-plane data.

2. In-plane Measurements

When we measure diffraction from a surface, the sample is usually the face of a massive crystal that would block the X-ray beam. If we require the incident and exit beams to enter and leave through the prepared face we have the geometry of Fig. 2. At small perpendicular momentum transfer ($l \approx 0$) we have the *grazing incidence* condition shown. The sample face is almost parallel to the diffraction plane and both beams make very small angles to it. Using the conventional definitions of the symmetric 4-circle diffractometer (Busing and Levy 1967), the sample angle is θ , the diffraction angle is 2θ , and the (small) tilt about an axis bisecting the incident and exit beams is χ . The tilt χ determines the incidence and exit angles, α and β (Fig. 2), which need to be slightly greater than zero, i.e.

$$\sin \alpha = \sin \beta = \sin \chi \sin \theta. \quad (1)$$

When α or β is near to α_c , the critical angle for total external reflection, X-ray refraction takes place and modifies the intensities as discussed by Vineyard (1982).

For in-plane I_{hk} measurements we need to define the equivalent of an *integrated intensity* (Warren 1969) which is to be analysed as the square of the structure factor.

Unfortunately, such a quantity is poorly defined because the diffraction is diffuse in the perpendicular direction. We must necessarily cut off some of the intensity with the slits of the diffractometer that define the resolution in the out-of-plane direction. This resolution is given by

$$\Delta q_v = \frac{2\pi}{\lambda} \frac{L}{D}, \quad (2)$$

where L is the slit height at distance D and λ is the X-ray wavelength. This is one of the experimental parameters that appears in the master formula for the integrated intensity given below.

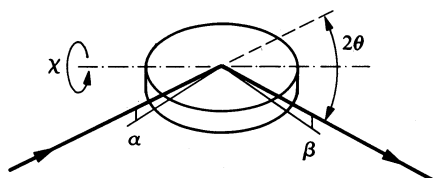


Fig. 2. Geometry for observing diffraction from the surface of the sample (disc) using the standard 4-circle convention of Busing and Levy (1967). Incident and exit angles α and β are controlled by the sample tilt angle χ (see equation 1).

Experimentally, integrated intensities are measured with an ω -scan in the same way as for bulk crystallography: the sample angle is rocked about the diffraction condition to obtain a certain total number of counts. Background, measured nearby in a similar manner, is then subtracted. The number of counts (above background) detected is I_{hk} . Starting from the Thomson scattering formula, it is possible to derive the following expression (Robinson 1987, based on Warren 1969):

$$I_{hk} = I_0 \frac{APR}{\Omega \sin 2\theta} |F_{hk}|^2, \quad (3)$$

where the variables are defined and discussed below. This master equation defines the various corrections which relate the surface integrated intensity I_{hk} to the surface structure factor amplitude F_{hk} :

- (a) I_0 contains the incident flux and a number of fundamental constants. Unless data are taken on an absolute scale, this will be a scale factor to emerge from fitting.
- (b) Ω is the angular velocity of the ω -scan in degrees per second or related units. Sometimes the speed is adjusted from peak to peak to improve statistics.
- (c) $\sin 2\theta$ is the normal Lorentz factor.
- (d) P is the polarisation factor which depends on the source, with $P = \frac{1}{2}(1 + \cos^2 2\theta)$ for an unpolarised source, $P = 1$ for a synchrotron radiation (SR) source and vertical scattering plane, and $P = \cos^2 2\theta$ with a SR source and horizontal plane.

- (e) A is the active surface area of the sample. This correction may depend on the scattering angle and sample orientation. For a small sample bathed in the incident beam and fully visible by the detector, the active scattering area is the total sample area, i.e. constant. More commonly, however, to avoid edge effects and to reduce background, the beams are slit down parallel to the plane. If L_1 and L_2 are the slit widths (1 to 2 mm typically) of the incident and diffracted beams and the sample is sufficiently large, then

$$A = L_1 L_2 / \sin 2\theta. \quad (4)$$

This is simply a formula for the area of the parallelogram of intersection of the two beams defined by the slits. At small 2θ the parallelogram can walk off the sample edges and a new and more relaxed area correction is needed.

- (f) R refers to the resolution effects mentioned above; here $R = \Delta q_v$.

Of these corrections to the integrated intensity, only the R and A factors should be unfamiliar to the 3D crystallographer. The former is usually constant and can be ignored for in-plane measurements, while the $\sin 2\theta$ dependence of the latter acts like a second Lorentz factor. The procedure implicit in equation (3) has been used in several in-plane surface structure determinations with success (Bohr *et al.* 1985; Feidenhans'l *et al.* 1987; Robinson *et al.* 1988). Agreement between calculated and observed intensities is in the 5–10% range. Almost all of this error is in the reproducibility of symmetry equivalent reflections and may be attributed to sample inhomogeneities. Systematic discrepancies that might indicate absent correction factors are not seen.

3. Out-of-plane Measurements

We now wish to generalise the results of the previous section to handle the collection of intensity data for the case of nonzero perpendicular momentum transfer. Relatively few attempts have been made to obtain this kind of data (Robinson 1983; Feidenhans'l *et al.* 1987) and the question of intensity corrections has not been addressed before. We will limit the discussion to the 4-circle diffraction geometry of Fig. 2 in which the detector remains in the scattering plane and the sample is inclined by means of the diffractometer angle χ . Feidenhans'l *et al.* (1987) used a geometry in which the sample remains flat and the detector moves out-of-plane; the corrections there will be different.

We resolve the momentum transfer q , that spans the reciprocal lattice, into components (q_{\parallel} , q_{\perp}) parallel and perpendicular to the surface. The diffractometer angles are then given by (Busing and Levy 1967)

$$2 \frac{2\pi}{\lambda} \sin \theta = (q_{\parallel}^2 + q_{\perp}^2)^{\frac{1}{2}}, \quad \tan \chi = q_{\perp} / q_{\parallel}. \quad (5, 6)$$

The crystallographic transformation from lattice indices hkl to momentum transfer is made in the usual way. For example in the W(001) case of Fig. 1, we have

$$q_{\parallel} = \frac{2\pi}{a_0} (h^2 + k^2)^{\frac{1}{2}}, \quad q_{\perp} = \frac{2\pi}{a_0} l, \quad (7a, b)$$

where a_0 is the cubic lattice constant (3.16 \AA).

Considering one by one the various factors of equation (3), we find changes necessary only in A and R to include the out-of-plane corrections. The former is easy to visualise, being the illuminated sample area that is in line of sight with the detector, as before. For the small beam, large sample case, we have

$$A' = \frac{L_1 L_2}{\sin 2\theta \cos \chi}, \quad (8)$$

where the extra $\cos \chi$ accounts for the elongation of the illuminated spot due to tilting the sample. If the beam size in the out-of-plane direction is not sufficiently tall, the signal will be cut off and equation (8) will have to be modified.

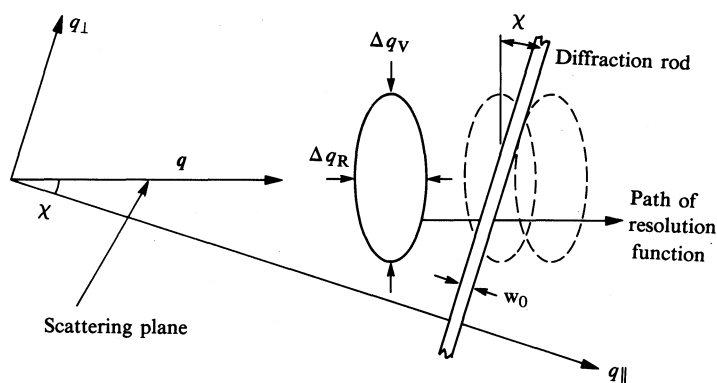


Fig. 3. Model of the trajectory of the resolution function (ellipse) as it passes a rod of surface diffraction on a radial (θ - 2θ) scan, parallel to the total momentum transfer q . Here Δq_R , Δq_V and Δq_T are the dimensions of the resolution ellipse along the principal axis directions of the diffractometer, which are aligned with the page; q_V and q_R refer to the sample coordinate frame; w_0 is the finite-size width of the rod.

Harder to see, however, are the effects of the resolution function, previously accounted for in the trivial factor of equation (2). There, $R = \Delta q_V$ represents the length of rod that is integrated in the ω -scan. When the rod tilts by an angle χ , it becomes misaligned with the resolution function and intensity is lost. This can be a dramatic effect when the resolution function is very long and thin as in a high-resolution diffractometer (Robinson 1985). We are going to approximate the resolution function in Fig. 3 by an ellipsoid of (reciprocal space) dimensions Δq_V perpendicular to the scattering plane, Δq_R parallel to the scattering plane in the radial direction (parallel to q) and Δq_T in the in-plane, transverse direction. We note that the surface plane is inclined at angle χ with respect to the scattering plane (Fig. 3). Here Δq_R and Δq_T are usually made small to obtain high resolution and good signal-to-background for sharp peaks. Typical values are $5 \times 10^{-4} \text{ \AA}^{-1}$ for a Si(111) resolution instrument, or $3 \times 10^{-2} \text{ \AA}^{-1}$ for graphite resolution. In equation (2), Δq_V is degraded deliberately to augment the signal rates (see equation 3) and is typically chosen to be 10^{-1} \AA^{-1} .

Fig. 3 shows what happens when a radial (θ - 2θ) scan is made through a rod tilted by angle χ . The observed width w is given by the convolution of the gaussian

resolution function (of widths Δq_R and Δq_V) with a tilted line:

$$w = \frac{1}{\cos \chi} (\Delta q_R^2 \cos^2 \chi + \Delta q_V^2 \sin^2 \chi)^{\frac{1}{2}}. \quad (9)$$

If the finite width of the rod w_0 is included as well, this adds in quadrature as

$$w' = \frac{1}{\cos \chi} (w_0^2 + \Delta q_R^2 \cos^2 \chi + \Delta q_V^2 \sin^2 \chi)^{\frac{1}{2}}. \quad (10)$$

It is clear how rapidly this changes, even for modest values of χ , since Δq_V is so much bigger than Δq_R .

Now we can calculate the effects of this on the integrated intensity obtained in an ω -scan: The resolution function passes perpendicular to the page in Fig. 3 and gives an intensity proportional to the length of its intersection with the tilted rod. The general result, including the effects of the finite rod width, is

$$R' = \frac{\Delta q_R \Delta q_V}{(w_0^2 + \Delta q_R^2 \cos^2 \chi + \Delta q_V^2 \sin^2 \chi)^{\frac{1}{2}}}. \quad (11)$$

In practice, the resolution parameters must be evaluated carefully to make this correction. A good consistency check is to verify the predictions of equation (10) first, as we demonstrate in the next section.

4. Application to the W(001) Surface

A full account of the crystallographic analysis of this surface has appeared elsewhere (Altman *et al.* 1988). The surface was prepared by heating a crystal to 2400 K in 10^{-10} Torr vacuum (1 Torr \equiv 133 Pa) in a special enclosure that mounts on a 4-circle diffractometer. Integrated intensities of the $(\frac{1}{2}, \frac{1}{2}, l)$, $(\frac{3}{2}, \frac{3}{2}, l)$, $(\frac{1}{2}, \frac{3}{2}, l)$ and $(\frac{3}{2}, \frac{5}{2}, l)$ rods of diffraction were measured in the range $0 < l < 1.5$ (approx.) to study multilayer reconstruction effects. A 60 kW rotating anode source was used with a graphite monochromator and analyser. A maximum of 14 counts per second above background was seen in the surface peaks. A preliminary analysis of the data (Robinson *et al.* 1987) showed good agreement with the model of Fig. 1c with displacements in two layers instead of one. A puzzling result was that the DW factor was very anisotropic, being ten times bigger perpendicular to the surface plane than within it. The B_l value of 4 \AA^2 was unrealistically large for purely vibrational motion. We now consider this value to be spurious because we had not appreciated the importance of the R' correction (equation 11).

The radial linewidths of three of the surface diffraction rods are plotted in Fig. 4 as a function of tilt angle χ , defined by equation (6). Also shown is a fit to equation (10) showing good agreement. The value of $\Delta q_R = 0.0122$ reciprocal lattice units (1 rlu $\equiv 1.99 \text{ \AA}^{-1}$) was known from the widths of bulk peaks. The fit values of $w_0 = 0.0150$ rlu and $\Delta q_V = 0.043$ rlu were obtained. When these numbers were used to correct the intensity data according to equations (11) and (3) the need for a large B_l disappeared (Altman *et al.* 1988) indicating the improvement. An isotropic B of $0.2 \pm 0.3 \text{ \AA}^2$ then described the data very well.

In conclusion, we have derived out-of-plane corrections to the intensity correction formula appropriate for surface X-ray crystallography, where the diffuse nature of the peaks affects the problem in a fundamental way. We have shown these to be valid for

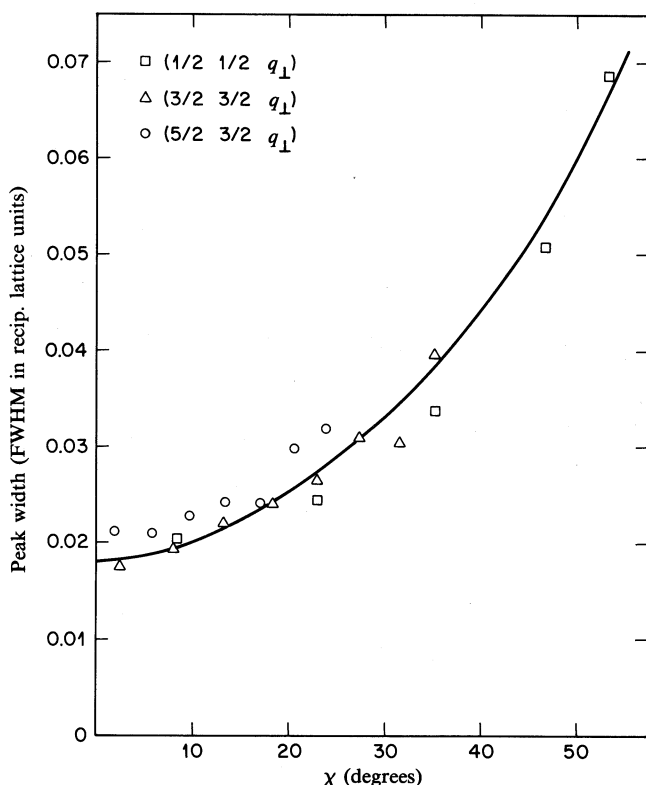


Fig. 4. Measured radial widths of surface diffraction rods for W(001) as a function of tilt angle χ . The fit is equation (10).

W(001) data. The new resolution correction (equation 11) is important with graphite resolution, but will be ten times more so for high-resolution instruments, such as commonly found at SR facilities. It may become necessary to measure surface diffraction intensities with both radial and ω -scans to make reliable integrations. This need is even more pressing when additional sources of error such as surface miscut or sample misorientation are considered.

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