

# Calculation of crystal truncation rod structure factors for arbitrary rational surface terminations

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The technique of crystal truncation rod (CTR) diffraction is widely used for studying the structure of crystalline surfaces and interfaces. The theory and experimental details of the technique are well established; however, published methods for structure-factor calculations are typically based on a simple surface cell geometry. A method is presented for determining a surface coordinate system which results in a reciprocal lattice that is simply defined in terms of the surface termination. Based on this surface coordinate system, a general formalism for the calculation of CTR structure factors is re-derived, which may be easily applied to any surface that can be represented as a rational plane of a bulk crystal system.

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## 1. Introduction

X-ray scattering techniques are broadly applied to the study of crystalline surface structures. Among the most common surface scattering techniques is the measurement of crystal truncation rods (CTRs). Crystal truncation rods are diffuse streaks of intensity running perpendicular to a surface connecting bulk Bragg points and arise as a natural consequence of the presence of a sharp termination of the crystal (Robinson, 1986; Andrews & Cowley, 1985). CTRs can be analyzed for the determination of surface termination, relaxation and surface roughness, as well as applied to the study of reconstructed surfaces by analysis of fractional order rods. The details of the measurements have been discussed previously (Fuoss & Brennan, 1990; Robinson & Tweet, 1992; Vlieg *et al.*, 1989) and the sensitivity of CTRs to the above surface properties has been shown for a number of systems (Feidenhans'l, 1989; Renaud, 1998; Robinson, 1991).

The conventional method for the analysis of CTRs is derived using a unit cell defined in terms of the surface orientation, with the unit-cell basis vectors defined by two in-plane lattice vectors and a third lattice vector perpendicular to the surface plane (Robinson, 1986; Vlieg, 2000; Vlieg *et al.*, 1989). This definition of the real-space lattice leads to a convenient representation of the reciprocal lattice in which the scattering vector ( $\mathbf{Q}$ ) is expressed in terms of two pure in-plane components ( $H_s, K_s$ ) which give the parallel momentum transfer ( $\mathbf{Q}_{\parallel}$ ), and a third component ( $L_s$ ) giving the perpendicular momentum transfer ( $\mathbf{Q}_{\perp}$ ).<sup>1</sup> The structure-factor calculations are then given in terms of summations over the in-plane and surface-normal directions.

<sup>1</sup> We use  $\mathbf{a}_s, \mathbf{b}_s, \mathbf{c}_s$  and  $H_s, K_s, L_s$  to refer, respectively, to the real-space basis vectors and the reciprocal-lattice indices of the scattering vector ( $\mathbf{Q}$ ) in the surface indexing.

For cubic lattices, a surface termination along a rational plane will always result in a suitable surface unit cell. However, in general, it may not be possible to define a surface unit cell with a basis vector along the direction of the surface normal that is space-filling (Robinson, 1998). Two approaches may be used to index a surface unit cell in which there is no rational repeat of the lattice along the direction of the surface normal. First, the surface cell indexing may be performed using two in-plane lattice vectors to define  $\mathbf{a}_s$  and  $\mathbf{b}_s$ , and a third out-of-plane lattice vector which is not perpendicular to the surface plane to define  $\mathbf{c}_s$ . In this case, the plane defined by the reciprocal-lattice vectors  $\mathbf{a}_s^*$  and  $\mathbf{b}_s^*$  will be tilted with respect to the surface plane, while  $\mathbf{c}_s^*$  is parallel to the surface-normal direction. In the second approach, two in-plane lattice vectors are again used to define  $\mathbf{a}_s$  and  $\mathbf{b}_s$ , but we now define  $\mathbf{c}_s$  to be mutually perpendicular. Again  $\mathbf{c}_s^*$  is parallel to the surface-normal direction, but the plane defined by  $\mathbf{a}_s^*$  and  $\mathbf{b}_s^*$  is now forced to be parallel to the surface plane. However, in this prescription  $\mathbf{c}_s$  is not necessarily a lattice vector of the bulk crystal.

In both surface indexing approaches, the CTRs are parallel to the  $\mathbf{c}_s^*$  direction. If  $\mathbf{c}_s$  is chosen as an off-normal bulk lattice vector, the surface cell will retain a well defined translational symmetry, but the positions of the Bragg peaks along the surface rods will not have a simple relationship with respect to the in-plane (*i.e.*  $\mathbf{Q}_{\perp} = 0$ ) position when the direction of  $\mathbf{Q}$  points across the surface. In the second approach,  $\mathbf{Q}$  is simply expressed in terms of two pure in-plane components ( $H_s, K_s$ ) and a single perpendicular ( $L_s$ ) component with  $L_s = 0$  corresponding to the in-plane position for all CTRs. This second approach results in a convenient coordinate system for data collection and analysis protocols; however, the introduction of a non-crystallographic unit cell must be taken into account in the calculation of the CTR profile. In this paper, we

explore the consequences of this second choice and show that it offers a viable way to perform calculations of CTR structure factors.

## 2. Definition of the surface basis system

For a crystalline surface that can be defined using a crystallographic right-parallelepiped unit cell, the entire crystal structure can be generated by translation of the unit cell using a lattice vector

$$\mathbf{R}_c = n_1 \mathbf{a}_s + n_2 \mathbf{b}_s + n_3 \mathbf{c}_s, \quad (1)$$

where the  $n$ 's are integers. The basis vectors  $\mathbf{a}_s$  and  $\mathbf{b}_s$  are in the surface plane and the third basis,  $\mathbf{c}_s$ , is parallel to the surface normal. The surface plane is taken to be at  $n_3 = 0$ , with  $n_3 < 0$  in the bulk, and the bulk crystal extends to  $n_3 = -\infty$ . The crystal is assumed to be of large extent in-plane with  $n_{1,2}$  spanning the range  $\pm(N_{1,2} - 1)/2$ . This geometry can be viewed as building up the crystal by stacking slabs of  $N_1 \times N_2$  cells along the direction normal to the surface, where  $n_{1,2,3} = 0$  defines the center of the surface plane. It is assumed that the slab stacking sequence is simply repeated, such that the lattice points ( $n_{1,2} = 0, n_3$ ) lie on the line perpendicular to the surface passing through the lattice origin at  $n_{1,2,3} = 0$ .

The surface coordinate frame used here maintains the above definition for the surface unit cell, with basis vectors  $\mathbf{a}_s$  and  $\mathbf{b}_s$  in the surface plane and  $\mathbf{c}_s$  parallel to the surface normal to define the two-dimensional slab that describes the surface of interest. However, we relax the condition that the slabs are simply repeated along the surface normal. Rather, we assume a more general case in which the remainder of the bulk crystal can be generated by repeat of the two-dimensional slabs along a slab repeat vector,  $\mathbf{V}_r$ , where  $\mathbf{V}_r$  is not necessarily parallel to the surface normal.

A more concise description of the surface indexing may be arrived at by defining the origin of the surface coordinate system to be coincident with the origin of the bulk lattice. We assume that the surface termination can be expressed as a rational plane ( $HKL$ ) of the bulk lattice. Therefore, the bulk

crystal will be terminated by the plane perpendicular to the surface-normal vector,  $\mathbf{d}_{HKL}/|\mathbf{d}_{HKL}|$ , centered at a distance  $|\mathbf{d}_{HKL}|$  from the lattice origin, where  $|\mathbf{d}_{HKL}|$  is the usual plane spacing as depicted in Fig. 1. We note that since the plane ( $HKL$ ) is a rational plane (where  $H, K, L$  are a set of relatively prime integers), it will always contain an infinite set of bulk lattice points, as will all planes parallel to ( $HKL$ ) centered at intervals of  $n\mathbf{d}_{HKL}$ , where  $n = 0, \pm 1, \pm 2, \dots$  (Kelly & Groves, 1970; Sands, 1982). Therefore, the in-plane basis vectors of the surface coordinate system ( $\mathbf{a}_s, \mathbf{b}_s$ ) can be chosen from the set of bulk lattice vectors in the plane parallel to ( $HKL$ ) passing through the system origin ( $n = 0$  in Fig. 1). The in-plane basis vectors are typically chosen as the two smallest non-collinear vectors that form a right-handed system with respect to  $\mathbf{d}_{HKL}$ , and can be expressed in terms of the bulk in-plane lattice vectors by

$$\mathbf{a}_s = x_{as} \mathbf{a} + y_{as} \mathbf{b} + z_{as} \mathbf{c} \quad (2)$$

and

$$\mathbf{b}_s = x_{bs} \mathbf{a} + y_{bs} \mathbf{b} + z_{bs} \mathbf{c}, \quad (3)$$

where  $[x_{as}, y_{as}, z_{as}]$  and  $[x_{bs}, y_{bs}, z_{bs}]$  are integers.

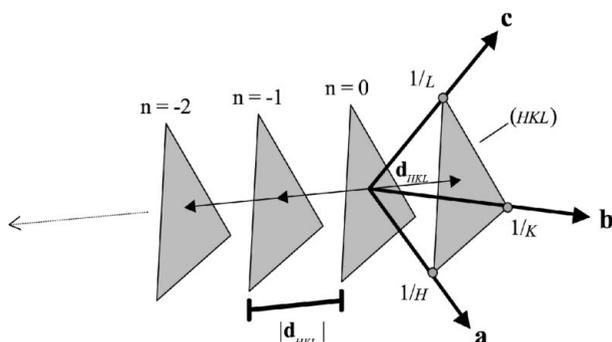
A space-filling unit cell may be defined using a third out-of-plane bulk lattice vector. However, the third lattice vector in this prescription will not necessarily be parallel to  $\mathbf{d}_{HKL}$  since the line parallel to  $\mathbf{d}_{HKL}$  is not always a rational line in non-cubic systems. Choosing an off-normal lattice vector for  $\mathbf{c}_s$  results in the plane defined by  $\mathbf{a}_s^*$  and  $\mathbf{b}_s^*$  being tilted with respect to the surface plane (defined by  $\mathbf{a}_s$  and  $\mathbf{b}_s$ ); therefore, the  $H_s$  and  $K_s$  components of  $\mathbf{Q}$  will have non-zero components in the direction of the surface normal.

In order to maintain the definition of  $\mathbf{Q}$  such that  $H_s$  and  $K_s$  are purely in-plane indices, we force  $\mathbf{c}_s$  to be oriented perpendicular to the surface plane. This will be a useful convention in the scattering formalism and ensures that  $L_s = 0$  corresponds to having a zero perpendicular component of the scattering vector. The basis transformation is then completed with the relation

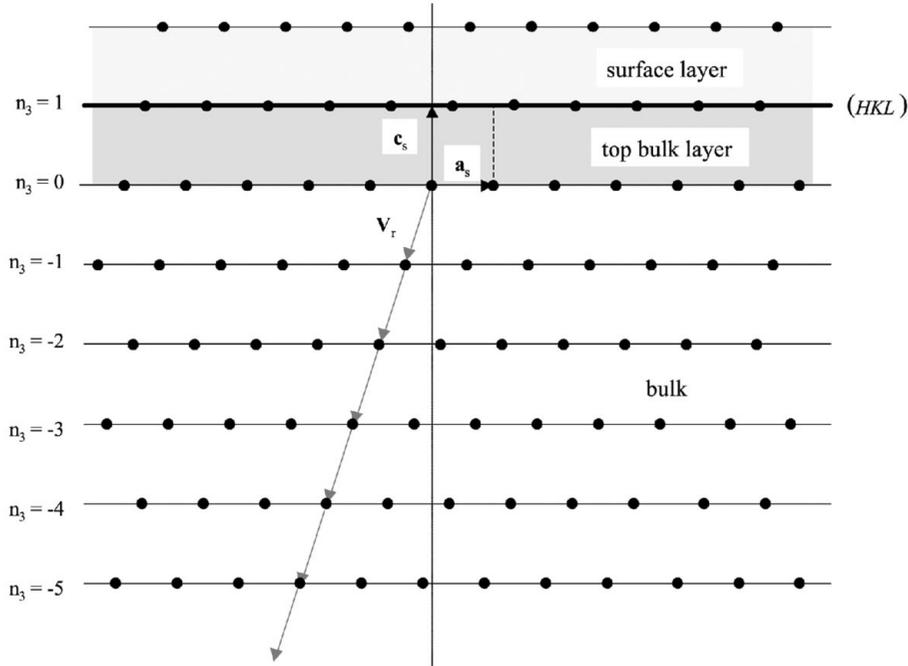
$$\mathbf{c}_s = x_{cs} \mathbf{a} + y_{cs} \mathbf{b} + z_{cs} \mathbf{c}, \quad (4)$$

where  $\mathbf{c}_s$  is parallel to  $\mathbf{d}_{HKL}$  and  $[x_{cs}, y_{cs}, z_{cs}]$  are not necessarily all integers.

The unit cell defined by this set of surface basis vectors is a crystallographic pseudo-cell owing to the potential lack of translational symmetry along the  $\mathbf{c}_s$  axis. However, it will give the correct two-dimensional net of cells defining the surface layer of the bulk crystal (Fig. 2, top bulk layer). The generation of a space-filling model then requires the introduction of an additional bulk lattice vector,  $\mathbf{V}_r$ , which describes the lattice repeat of the surface coordinate system (Fig. 2). Therefore,  $\mathbf{V}_r$  is a vector from the common origin of the bulk and surface coordinate systems which terminates at a bulk lattice point on a plane parallel to ( $HKL$ ) positioned at  $-n\mathbf{d}_{HKL}$ , where  $n = 1, 2, 3, \dots$  refers to the  $n$ th plane below the surface origin (Fig. 1). The magnitude of  $\mathbf{V}_r$  projected onto the line perpendicular to the surface then defines the magnitude of  $\mathbf{c}_s$ , which results in  $|\mathbf{c}_s| = n|\mathbf{d}_{HKL}|$ , and  $\mathbf{c}_s = n\mathbf{d}_{HKL}$  can be substituted into equation



**Figure 1** Surface plane ( $HKL$ ) defined in the bulk basis system ( $\mathbf{a}, \mathbf{b}, \mathbf{c}$ ). The origin of the surface system is taken to be the same as the bulk, and the plane ( $HKL$ ), which makes the intercepts  $1/H, 1/K$  and  $1/L$  with  $\mathbf{a}, \mathbf{b}$  and  $\mathbf{c}$ , respectively, defines the crystal surface. Planes parallel to ( $HKL$ ) spaced at  $|\mathbf{d}_{HKL}|$  are defined with the index  $n$ , with  $n \leq 0$  corresponding to planes within the bulk crystal.



**Figure 2**

Surface coordinate system defined in the bulk real-space lattice. Solid dots are bulk lattice points. The vectors  $\mathbf{a}_s$  and  $\mathbf{b}_s$  (which would point out of the plane of the paper) are the bulk lattice vectors that define the in-plane basis vectors in the surface coordinate system. The vector  $\mathbf{c}_s$  is the third surface basis vector and is taken parallel to the surface normal (dotted line). The plane  $(HKL)$  at  $n_3 = 1$  corresponds to the termination of the bulk crystal. The layer of surface cells at  $n_3 = 0$  defines the top layer of the bulk crystal, and layers at  $n_3 \leq 0$  are within the bulk crystal. The slab repeat vector,  $\mathbf{V}_r$ , is the bulk lattice vector which describes the repeat of the surface unit cell within the bulk. An additional layer of cells at  $n_3 = 1$  is included to account for differences in stoichiometry or structure of the surface relative to the bulk material.

(4). A reasonable choice for  $\mathbf{V}_r$  can be found from considering the lattice points to the first several planes from the origin into the bulk and choosing the bulk lattice vector that makes the smallest angle with the vector  $-\mathbf{d}_{HKL}$  (Fig. 2).

We note that in these calculations the explicit form of  $\mathbf{d}_{HKL}$  is required. The coefficients of this vector in the bulk real-space basis can be found from the reciprocal-lattice vector  $\mathbf{H}_{HKL} = [H, K, L]$  using the transformation

$$\mathbf{d}_{HKL} = (g)^{-1} \mathbf{H}_{HKL} / |\mathbf{H}_{HKL}|^2, \quad (5)$$

where

$$g = \begin{pmatrix} \mathbf{a} \cdot \mathbf{a} & \mathbf{a} \cdot \mathbf{b} & \mathbf{a} \cdot \mathbf{c} \\ \mathbf{b} \cdot \mathbf{a} & \mathbf{b} \cdot \mathbf{b} & \mathbf{b} \cdot \mathbf{c} \\ \mathbf{c} \cdot \mathbf{a} & \mathbf{c} \cdot \mathbf{b} & \mathbf{c} \cdot \mathbf{c} \end{pmatrix} \quad (6)$$

is the metric tensor for the bulk lattice. Therefore, having defined the vectors in bulk basis system which describe the basis vectors and basis repeat for the surface coordinate system, we can define the basis transformation matrix,  $M$ , where

$$M = \begin{pmatrix} x_{as} & y_{as} & z_{as} \\ x_{bs} & y_{bs} & z_{bs} \\ x_{cs} & y_{cs} & z_{cs} \end{pmatrix} \quad (7)$$

and the transformation

$$\mathbf{V}_{r,s} = (M^T)^{-1} \mathbf{V}_r \quad (8)$$

gives the coefficients of  $\mathbf{V}_r$  in the surface basis system. This enables us to give a general form for the slab repeat vector in the surface basis:

$$\mathbf{V}_{r,s} = n_3 \Delta_1 \mathbf{a}_s + n_3 \Delta_2 \mathbf{b}_s + n_3 \mathbf{c}_s, \quad (9)$$

where the absolute values of  $\Delta_1$  and  $\Delta_2$  are determined from equation (8). The integer index  $n_3$  is now the slab index, where  $n_3 = 0$  refers to the slab that terminates the bulk crystal, and  $n_3 < 0$  refers to slabs within the bulk crystal (Fig. 2).

Given the definition of the surface basis system above, the coordinates of atom  $j$  in cell  $(n_1, n_2, n_3)$  are given by the vector (in the surface coordinate frame)

$$\mathbf{R}_{j,s} = \mathbf{r}_{j,s} + \mathbf{R}_{i,s}(n_{1,2}) + \mathbf{V}_{r,s}(n_3), \quad (10)$$

where the  $n$ 's are integers ( $n_3 \leq 0$ ) and  $\mathbf{r}_{j,s}$  gives the fractional coordinates of atom  $j$  in the unit cell defining the origin. The vector  $\mathbf{R}_{i,s}(n_{1,2})$  gives the in-plane coordinates for the origin of cell  $(n_1, n_2)$  in the  $n_3$  slab,

$$\mathbf{R}_{i,s}(n_1, n_2) = n_1 \mathbf{a}_s + n_2 \mathbf{b}_s, \quad (11)$$

and  $\mathbf{V}_{r,s}$  gives the origin of cell  $(n_{1,2} = 0, n_3)$ .

Deriving the reciprocal lattice based on the definition of the surface system real-space basis vectors, the scattering vector is given by

$$\mathbf{Q} = 2\pi(H_s \mathbf{a}_s^* + K_s \mathbf{b}_s^* + L_s \mathbf{c}_s^*), \quad (12)$$

where  $H_s$  and  $K_s$  give the degree of momentum transfer in the surface plane and  $L_s$  gives the degree of momentum transfer

along the surface normal. The indices of a reciprocal-lattice vector can be transformed from the bulk to the surface indexing using the transformation

$$\begin{pmatrix} H_s \\ K_s \\ L_s \end{pmatrix} = M \begin{pmatrix} H \\ K \\ L \end{pmatrix} \quad (13)$$

and the reciprocal relation is given using the inverse of  $M$ . We note that the reciprocal-lattice vectors describing bulk Bragg points in the bulk indexing may have non-integer  $L_s$  values in the surface indexing described above. However, a relationship is provided below that easily allows the determination of Bragg peak positions along a CTR.

### 3. Structure-factor calculations

We assume here that the scattering experiment is carried out in the Bragg geometry using a ‘thick’ sample with a single well defined surface through which the incident and reflected X-rays penetrate (Robinson, 1986). The intensity of the scattered radiation measured at the detector is proportional to the square of the magnitude of the structure factor,  $I \propto |F|^2$ . The structure factor may be written as a sum over all atoms in the bulk sample (Warren, 1969):

$$F_b = \sum f_j \exp(i\mathbf{Q} \cdot \mathbf{R}_j) \exp[B_j(|\mathbf{Q}|/4\pi)^2], \quad (14)$$

where  $f_j$  is the scattering factor for atom  $j$ ,  $\mathbf{R}_j$  is the position of atom  $j$  in the sample, and  $B_j$  is the thermal disorder parameter. Using the surface coordinate system defined above (Fig. 2), the product  $\mathbf{Q} \cdot \mathbf{R}_j$  may be calculated using equation (10) for  $\mathbf{R}_j$  and equation (12) for  $\mathbf{Q}$ , which yields

$$\mathbf{Q} \cdot \mathbf{R}_j = \mathbf{Q} \cdot \mathbf{r}_{j,s} + \mathbf{Q} \cdot \mathbf{R}_{i,s} + \mathbf{Q} \cdot \mathbf{V}_{r,s}, \quad (15)$$

where the first term is independent of  $n_{1,2,3}$ , the second term depends on  $n_{1,2}$  and the third term depends only on  $n_3$ . Substitution of equation (15) into equation (14) gives

$$F_b = F_{bc} \left[ \sum_{n_1=-(N_1-1)/2}^{(N_1-1)/2} \sum_{n_2=-(N_2-1)/2}^{(N_2-1)/2} \exp(i\mathbf{Q} \cdot \mathbf{R}_{i,s}) \right] \times \left[ \sum_{n_3=-\infty}^0 \exp(i\mathbf{Q} \cdot \mathbf{V}_{r,s}) \exp(\alpha n_3) \right], \quad (16)$$

where  $N_1$  and  $N_2$  are the numbers of unit cells along the in-plane basis vectors ( $\mathbf{a}_s$  and  $\mathbf{b}_s$ ), and the third summation is over all slabs of the bulk crystal. The factor  $\alpha$  accounts for attenuation of the beam as a function of depth into the crystal and is given by  $\alpha = \mu|\mathbf{c}_s|$ , where  $\mu$  is the mass absorption coefficient.  $F_{bc}$  is the structure factor for the unit cell, given by

$$F_{bc} = \sum_{j=1}^m f_j \exp(i\mathbf{Q} \cdot \mathbf{r}_{j,s}) \exp[B_j(|\mathbf{Q}|/4\pi)^2], \quad (17)$$

where  $\mathbf{r}_{j,s}$  is the coordinate of atom  $j$  in the unit cell (in the surface basis system) and the sum is over all  $m$  atoms in the unit cell. The structure factor for total scattering by the bulk terminated sample given by equation (16) has three independent terms arising from, respectively, the coordinates of

the atoms in the unit cell ( $F_{bc}$ ), the two-dimensional periodicity of cells in the slabs, and the stacking sequence of the slabs. The summations over  $n_1$  and  $n_2$  in equation (16) are the typical slit functions, where  $\mathbf{Q} \cdot \mathbf{R}_{i,s} = 2\pi(n_1H_s + n_2K_s)$ , and for integer  $H_s$  and  $K_s$  give  $N_1$  and  $N_2$ , respectively. Finally, given the product  $\mathbf{Q} \cdot \mathbf{V}_{r,s} = 2\pi(n_3\Delta_1H_s + n_3\Delta_2K_s + n_3L_s)$ , the sum over  $n_3$  can be written as

$$F_{\text{CTR}} = \sum_{n_3=-\infty}^0 \exp[i2\pi(\Delta_1H_s n_3 + \Delta_2K_s n_3 + n_3L_s)] \exp(\alpha n_3) = 1/[1 - \exp[-i2\pi(\zeta)] \exp(-\alpha)], \quad (18)$$

where  $\zeta = \Delta_1H_s + \Delta_2K_s + L_s$ . We note that if  $\Delta_1$  and  $\Delta_2$  are zero, corresponding to a crystallographic right-parallelepiped surface unit cell, we recover the usual form of  $F_{\text{CTR}}$  (Vlieg, 2000; Vlieg *et al.*, 1989). In the limit  $\alpha \rightarrow 0$ , the magnitude of  $F_{\text{CTR}}$  is given by  $|F_{\text{CTR}}|^2 = 1/[4 \sin^2(\pi\zeta)]$ , which is infinite for integer values of  $\zeta$ . Therefore, we identify integer  $\zeta$  values as bulk Bragg points and for integer ( $H_s, K_s$ ), the values of  $L_s$  corresponding to bulk Bragg points along a reciprocal-lattice rod running perpendicular to the surface are given by

$$L_s = \zeta - \Delta_1H_s - \Delta_2K_s, \quad (19)$$

where  $\zeta = 0, \pm 1, \pm 2 \dots$

Therefore, the total scattering intensity from a bulk terminated sample is given by

$$I \propto |F_b|^2 = N_1^2 N_2^2 |F_{bc} F_{\text{CTR}}|^2, \quad (20)$$

where systematic absences will be correctly handled by the corresponding value of  $F_{bc}$ . For integer  $H_s$  and  $K_s$ , there will be a smooth drop in the scattering intensity as a function of  $L_s$  away from a bulk Bragg reflection,  $I \propto |F_{bc}|^2/[4 \sin^2(\pi\zeta)]$ , which gives the typical CTR profile as a function of perpendicular momentum transfer.

### 4. Modified surfaces

To account for differences in stoichiometry or structure of the surface relative to the bulk, an additional layer of cells is included on top of the bulk terminated crystal at  $n_3 = 1$ , as shown in Fig. 2. We assume that this layer maintains the same lattice parameters as the transformed bulk system [for reconstructed surfaces the bulk cell may be defined in terms of the reconstruction so that the surface and bulk maintain the same lattice parameters (*cf.* Vlieg, 2000)]. The intensity of the scattering from the surface layer alone is proportional to the surface structure factor, which can be calculated using equation (16) with  $n_3 = 1$  and  $\mathbf{r}_{j,s}, f_j$  and  $B_j$  referring to the atoms in the surface-layer unit cell, which gives

$$F_s = F_{sc} \exp(i2\pi\zeta) \sum_{n_1=-(N_1-1)/2}^{(N_1-1)/2} \exp(i2\pi n_1 H_s) \times \sum_{n_2=-(N_2-1)/2}^{(N_2-1)/2} \exp(i2\pi n_2 K_s), \quad (21)$$

where  $F_{sc}$  is the structure factor for the surface unit cell [equation (17)]. The additional phase factor of  $\exp(i2\pi\zeta)$

simply shifts the fractional coordinates of the atoms to correspond to the  $n_3 = 1$  layer, and we have ignored the attenuation of the X-rays in the first layer. The two summations over  $n_1$  and  $n_2$  are again the typical slit functions and give  $N_1$  and  $N_2$ , respectively, for integer  $H_s$  and  $K_s$ . Therefore, equation (21) simplifies to

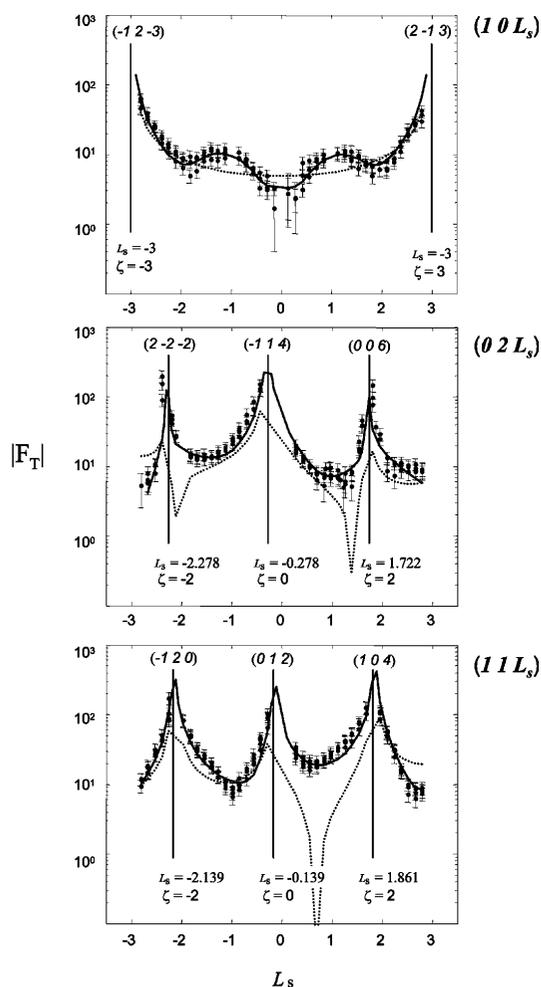
$$F_s = N_1 N_2 F_{sc}, \quad (22)$$

where the term  $\exp(i2\pi\zeta)$  is included in  $F_{sc}$ . The total structure factor is then given by the complex sum of the bulk and surface structure factors,

$$F_T = F_b + F_s = N_1 N_2 (F_{bc} F_{CTR} + F_{sc}), \quad (23)$$

and the measured intensity  $I$  will be proportional to  $N_1^2 N_2^2 |F_T|^2$ .

Modifications in the structure and/or composition of the surface with respect to the bulk will be expressed in the  $F_{sc}$  term; therefore, the interference between the scattering from the surface layer and that of the bulk will result in a structure along the rod profiles that is different from that expected for the bulk termination. The most surface-sensitive parts of the rod will be for perpendicular momentum transfer ( $L_s$ ) between bulk Bragg peaks, since this is where  $F_{CTR}$  approaches a minimal value.



**Figure 3** Experimental structure factors ( $F_T$ ) as a function of perpendicular momentum transfer ( $L_s$  in reciprocal-lattice units) for the  $\alpha$ - $\text{Al}_2\text{O}_3$  ( $1\bar{1}02$ ) surface. Structure factors were measured at beamline X16a at the NSLS, and are corrected for active area, polarization, step size and Lorentz factor (Robinson, 1991). The solid line is the best-fit model in which the atoms in the surface cell are allowed to relax from their bulk positions. Also fitted are the atom occupancies, Debye–Waller factors and overall roughness and scale factors. The dotted line is the calculated profile for the bulk un-relaxed termination. The rod index in the surface coordinate system is shown in bold. The solid vertical lines correspond to the positions of bulk Bragg reflections, with the bulk index shown above the line. Below the line are the values of  $L_s$  and  $\zeta = \Delta_1 H_s + \Delta_2 K_s + L_s$ , where  $\Delta_1 = 0$  and  $\Delta_2 = 0.1391$ . Additional experimental details are given elsewhere (Trainor *et al.*, 2002).

### 5. Example

The  $\alpha$ - $\text{Al}_2\text{O}_3$  ( $1\bar{1}02$ ) surface is used as a brief example of the method outlined above. The cell parameters for the bulk hexagonal unit cell are  $|\mathbf{a}| = 4.757$  and  $|\mathbf{c}| = 12.988$  Å (Kirkel & Eichhorn, 1990). The unreconstructed ( $1\bar{1}02$ ) surface is characterized by a rectangular surface mesh with  $\mathbf{a}_s$  defined by the  $[1\ 1\ 0]$  vector and  $\mathbf{b}_s$  defined by the  $[-1/3\ 1/3\ 1/3]$  vector in the bulk indexing ( $|\mathbf{a}_s| = 4.757$ ,  $|\mathbf{b}_s| = 5.127$  Å). The repeat vector is chosen as  $\mathbf{V}_r = [-2/3\ 2/3\ -1/3]$ , which terminates at the  $n = -2$  plane, and is approximately  $5.9^\circ$  off the surface-normal axis. Therefore, normal to the surface we have  $|\mathbf{c}_s| = 6.957$  Å ( $= 2|\mathbf{d}_{(1\bar{1}2)}|$ ), which gives a cell containing 20 atoms (four  $\text{Al}_2\text{O}_3$  units) and ten atomic layers thick. The choice of a cell thickness of  $2|\mathbf{d}_{(1\bar{1}2)}|$  was made to allow for relaxations several atomic layers deep into the surface unit cell. We note that the fractional indices in the vectors given for  $\mathbf{b}_s$  and  $\mathbf{V}_r$  are bulk lattice vectors for the non-primitive hexagonal indexing of  $\alpha$ - $\text{Al}_2\text{O}_3$  and these vectors have all integer indices if transformed to the primitive rhombohedral cell (Kelly & Groves, 1970). Substitution of the vectors defining  $\mathbf{a}_s$ ,  $\mathbf{b}_s$  and  $\mathbf{c}_s$  into equation (7) gives the transformation matrix

$$M = \begin{pmatrix} 1 & 1 & 0 \\ -1/3 & 1/3 & 1/3 \\ 0.713 & -0.713 & 0.287 \end{pmatrix} \quad (24)$$

and the indices of the repeat vector in the surface basis calculated from equation (8) are  $\Delta_1 = 0$  and  $\Delta_2 = 0.1391$ .

The experimental rod profiles along with calculated profiles for the bulk un-relaxed termination and best-fit surface model are depicted in Fig. 3. The experimental details and model description are discussed elsewhere (Trainor *et al.*, 2002). In Fig. 3, the indices of the Bragg reflections in the bulk indexing are shown, along with the corresponding values of  $\zeta$ . The profiles are calculated according to equation (23) using the surface system basis vectors defined in equation (24), and an additional surface cell at  $n_3 = 1$  was included to allow for relaxation of the surface structure. A good fit to the data was arrived at through adjustment of the structural parameters in the  $F_{sc}$  term of equation (23), with the parameters for the bulk structure factor fixed.

## 6. Conclusions

We have presented a method for determining a consistent surface coordinate system for surface-diffraction experiments and, based on this geometry, derived a simple generalization for the calculation of CTR structure factors. This approach allows similar data collection and analysis procedures to be applied to any crystal surface that can be represented as a rational plane of a bulk crystal system. However, the model presented here is based on a crystallographic pseudo-cell that requires the definition of an additional repeat vector ( $\mathbf{V}_r$ ) and may result in having bulk Bragg reflections occur at non-integer  $L_s$  positions.

An alternative indexing approach in which  $\mathbf{c}_s$  is defined with an off-normal lattice vector may be used to define a crystallographic surface unit cell. However, the surface indexing presented in this work is convenient for surface-diffraction experiments since it forces the components of all real- and reciprocal-space vectors to be expressed in terms of basis vectors that are parallel and perpendicular to the surface plane. Therefore, the CTRs arising from a rational termination of a crystal are always indexed using integer indices ( $H_s$  and  $K_s$ ) to define the in-plane component of the scattering vector ( $\mathbf{Q}_{\parallel}$ ) and a single continuous variable ( $L_s$ ) which gives the component of the scattering vector perpendicular to the surface plane ( $\mathbf{Q}_{\perp}$ ). The zero perpendicular momentum transfer always corresponds to  $L_s = 0$ , thus eliminating the need for a separate calculation for each rod as would be the case if a non-perpendicular  $\mathbf{c}_s$  were chosen.

Furthermore, this approach allows surface-atom relaxations, as well as anisotropic Debye–Waller factors, to be treated in a straightforward manner in model calculations. Typically the relaxation of surface atoms is greatest in the direction perpendicular to the surface plane, while in-plane motions may be constrained by the plane-group symmetry of the surface. Since the atomic fractional coordinates are defined in terms of directions parallel and perpendicular to the

surface, a single modeling approach consistent with established routines (*cf.* Vlieg, 2000) is easily applied to any rational surface termination. Detailed information on the surface termination and relaxation can be found from model fits to the CTR data, where occupancies, atomic coordinates and thermal disorder parameters in  $F_{sc}$  are used as floating variables. Additional details of CTR analysis, such as inclusion of surface roughness, multiple domains or multiple surface cells, are treated in the same fashion as described previously (Vlieg, 2000).

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