ROD: a program for surface X-ray crystallography

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A brief description is given of the C-program *ROD* with which surface structures can be refined on the basis of X-ray data. All main features one encounters on surfaces, like roughness, relaxations, reconstructions and multiple domains, are taken into account. The program has proven to be a useful tool over the past ten years.

1. Introduction

The determination of surface structures using X-ray diffraction has become increasingly popular with the emergence of ever more powerful synchrotron radiation sources. Most experiments have been performed on surfaces in vacuum, but the technique has also found applications in the determination of interfaces buried beneath a solid (Robinson *et al.*, 1988) or liquid (De Vries, Goedtkindt *et al.*, 1998). Few other techniques are available for this latter type of studies. The technique closely resembles bulk X-ray crystallography; the main differences are the weakness of the diffracted signal and the two-dimensional nature of the diffraction features. Reviews of the technique have been presented by Feidenhans'l (1989), Robinson (1991), Vlieg & Robinson (1992) and Robinson & Tweet (1992).

Existing bulk-crystallographic programs are less suitable for surface crystallography, mainly because with such programs it is difficult to describe the continuous intensity distribution along rods perpendicular to the surface and because it is difficult to take the surface roughness into account properly. This is the reason why a program was written especially for surface crystallography. Its name, *ROD*, points to the two-dimensional nature of the diffraction features. The present paper describes the basics of *ROD*; for a more comprehensive description the reader is referred to the manual (Vlieg, 1999).

2. Structure-factor calculation

2.1. Basics

The way in which the various calculations are performed in *ROD* closely resembles the formalism presented by Vlieg *et al.* (1989). The most essential part of *ROD* is the calculation of the structure factor of the surface. A structure factor is defined as

$$F_{hkl} = \sum_j f_j \exp[-B_j Q^2/(16\pi^2)] \exp[2\pi i(hx_j + ky_j + lz_j)], \quad (1)$$

with f_j the atomic scattering factor of atom j, B the Debye–Waller parameter, Q the total momentum transfer, (hkl) the Miller indices and $(xyz)_j$ the position of atom j in fractional coordinates. For bulk crystallography, the summation would go over all atoms in the bulk unit cell. For surface X-ray diffraction, we have to deal with two 'unit cells': (i) all atoms defined to be in the surface and (ii) all atoms in the bulk (see Fig. 1). The convention normally used in surface diffraction is that the lattice parameters $\mathbf{a}_1$ and $\mathbf{a}_2$ of the surface unit cell lie in the surface plane and that $\mathbf{a}_3$ points outwards. Then the Miller index l is along the out-of-plane direction. The size of $\mathbf{a}_3$ would be arbitrary for the surface unit cell (there is no true periodicity along that direction),

but is taken to be the same as that of the (well defined) bulk cell. The surface may consist of the same type of atoms with the same in-plane symmetry as in the bulk (in the case of relaxations), but may also have a different symmetry and/or contain different atoms (reconstruction, possibly caused by adatoms).

The total structure factor is given by the coherent sum of both contributions:

$$F_{sum} = F_{surf} + F_{bulk}, \quad (2)$$

with

$$F_{surf} = \sum_j^{\substack{\text{surface} \\ \text{unit cell}}} f_j \theta_j \exp[-B_j Q^2/(16\pi^2)] \exp[2\pi i(hx_j + ky_j + lz_j)], \quad (3)$$

$$F_{bulk} = \sum_{j=-\infty}^{0} F_u \exp(2\pi ilj) \exp(j\alpha) \quad (4)$$

and

$$F_u = \sum_j^{\substack{\text{bulk} \\ \text{unit cell}}} f_j \exp[-B_j Q^2/(16\pi^2)] \exp[2\pi i(hx_j + ky_j + lz_j)]. \quad (5)$$

An occupancy parameter θ is included in the definition of F_{surf} because in the surface unit cell not all positions need to be fully occupied. Note that the bulk and surface contributions can only be added coherently if the intensity is properly integrated (Vlieg *et al.*, 1989). The coordinates of the surface and bulk atoms should be expressed with respect to a common origin. It is important to define the unit cells such that the surface unit cell starts exactly above the bulk unit cell. The surface unit cell can be chosen to extend arbitrarily deep into the 'bulk'. For example, in Fig. 1 the line dividing surface and bulk could be lowered by half a bulk lattice spacing. This
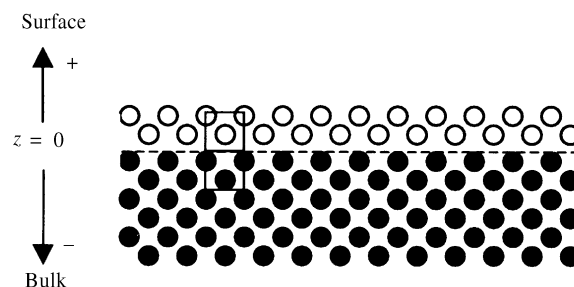

Figure 1
Schematic of a surface layer on top of a bulk crystal that is assumed to extend to minus infinity. Unit cells (of equal size) for both sides are indicated by outlined squares.

increases the amount of layers in the surface unit cell from two to three in this example. In that case one has to choose the two layers immediately below the surface cell to form the bulk unit cell. When the atoms in this extra 'surface' layer are kept at their bulk positions, the calculated diffracted intensity will remain unchanged. Note that the intensity is proportional to the square of the structure factor.

F_{bulk} describes the bulk-unit-cell structure factors F_u summed from the top layer to $-\infty$. Because of the attenuation factor α, only a finite amount of unit cells contributes to F_{bulk}. The summation (4) leads to

$$F_{bulk} = F_u/[1 - \exp(-2\pi il)\exp(-\alpha)]. \qquad (6)$$

F_{bulk} is the structure factor of a so-called crystal truncation rod (Robinson, 1986). At integer values for l it has a very high intensity, but, because of the termination of the crystal at a sharp interface, even for non-integer l values there is a finite intensity. For non-integer l, the attenuation factor α has only a very small effect on F_{bulk}. Depending on F_u, not all integer l values need to correspond to a maximum. The atomic positions in the bulk unit cell are assumed to be fixed in ROD.

For a reconstructed surface, so-called fractional-order reflections will occur. Expressed in the bulk lattice vectors, such reflections have non-integer h and/or k indices. At such positions the bulk contribution is zero and the total structure factor equals F_{surf}. ROD has no problem calculating structure factors for fractional indices, but in general it is better to keep the in-plane Miller indices as integers by defining a larger unit cell, e.g. for a (2×1) reconstruction, $(n/2, m)$ reflections would occur in terms of the bulk unit cell with lattice parameters $\mathbf{a}_1$ and $\mathbf{a}_2$. Choosing lattice parameters $2\mathbf{a}_1$ and $\mathbf{a}_2$ leads to a notation in which $(2n + 1, m)$ reflections originate exclusively from the surface, while $(2n, m)$ reflections are the interference sum of surface and bulk contributions. Only by choosing the larger lattice parameters does one use a genuine *unit cell*. In the larger unit cell, the bulk unit cell will have twice the number of atoms (or a different factor for a different reconstruction). It is important to give all the atoms in the bulk unit cell the proper in-plane coordinates, because only then will the bulk contribution cancel for 'fractional-order' reflections. It is thus often convenient to use a reconstructed unit cell and integer indices during data acquisition and analysis. When publishing the results, typically all indices are converted back to the non-reconstructed cell.

2.2. General surfaces

Often, a surface or interface does not consist of a single domain on top of a perfectly smooth bulk substrate. The following situations are treated in ROD:

(i) the surface layer covers the bulk only partly;

(ii) several symmetry-related surface unit cells are present;

(iii) the crystal (bulk + surface) is rough.

(The rare case of two different surface unit cells will not be discussed here, but interested readers are referred to the manual.) In order to include these situations, we need to define the following parameters:

S, scale factor;

R, roughness factor $(0 \leq R \leq 1)$;

f_s, fraction of crystal that is covered by surface layer $(0 \leq f_s \leq 1)$;

N_d, total number of symmetry-related surface domains;

α_j, occupancy of domain j.

When calculating F_{sum}, the following structure factors play a role:

$F_{b,j}$, structure factor of the jth domain of the bulk;

$F_{s,j}$, structure factor of the jth domain of the surface unit cell.

The important structure factors are now:

$$F_{bulk} = SR\left[\sum_j^{N_d} \alpha_j F_{b,j}^2 \right]^{1/2}, \qquad (7)$$

$$F_{surf} = SR\left[f_s \sum_j^{N_d} \alpha_j F_{s,j}^2 \right]^{1/2} \qquad (8)$$

and

$$F_{sum} = SR\left[(1 - f_s) \sum_j^{N_d} \alpha_j F_{b,j}^2 + f_s \sum_j^{N_d} \alpha_j (F_{s,j} + F_{b,j})^2 \right]^{1/2}. \qquad (9)$$

ROD always computes all three structure factors simultaneously. In these expressions, it is assumed that the symmetry-related domains are completely uncorrelated and that therefore their contributions add incoherently. Depending on the distribution of the domains, it may also be necessary to add the various contributions coherently. In that case, first the summation is performed and after that the result is squared:

$$F_{sum,coh} = SR\left\{ (1 - f_s)\left(\sum_j^{N_d} \alpha_j F_{b,j} \right)^2 + f_s\left[\sum_j^{N_d} \alpha_j (F_{s,j} + F_{b,j}) \right]^2 \right\}^{1/2}. \qquad (10)$$

ROD allows the choice of either of these situations.

2.2.1. Surface roughness. Surface roughness always leads to a decrease in intensity. The roughness models used in ROD all lead to a single roughness factor R, presented above, that is a simple multiplication factor of the smooth value. A simple roughness model is the so-called β model, in which surface level n has an occupancy β^n. Robinson (1986) derived the following expression for R for the case of a simple cubic crystal:

$$R_{\beta,cubic} = (1 - \beta)/[(1 - \beta)^2 + 4\beta \sin^2(\pi l)]^{1/2}. \qquad (11)$$

For non-cubic crystals, or when *within* a unit cell the occupancy varies from layer to layer, the calculation becomes more complicated. A formula that is nevertheless valid in many cases is

$$R_\beta = (1 - \beta)\{(1 - \beta)^2 + 4\beta \sin^2[\pi(l - l_{Bragg})/N_{layers}]\}^{1/2}, \qquad (12)$$

where l_{Bragg} is the l value of the nearest Bragg peak and N_{layers} is the number of layers in the unit cell. Equation (12) works fine if N_{layers} denotes the number of *equidistant* layers within the unit cell. This situation is described within ROD as 'approximated beta'.

All the other models available in ROD calculate the occupancies numerically, and are thus somewhat slower. It is therefore convenient to use equation (12) until proven otherwise. The numerical models use a column approximation, i.e. they assume that all layers have an identical termination. When these models are used, there is no need for the l_{Bragg} parameter. The atoms in the bulk unit cell need to be properly ordered, because the program determines the layer spacing vector $\mathbf{R}_{layer}$ from this bulk cell and the value of N_{layer}. The phase shift going from one layer to the next is $\psi_{hkl} = \mathbf{R}_{layer} \cdot \mathbf{H}$. The total structure factor is then the sum over identical column structure factors F_{column} shifted by the appropriate phase factor:

$$F_{tot} = F_{column} \sum_n \exp(in\psi_{hkl}). \qquad (13)$$

The reduction factor due to the roughness is now

$$R = \left| \sum_n \exp(in\psi_{hkl}) \right|^{1/2}. \qquad (14)$$

Various roughness models are available, such as Poissonian, Gaussian and two-level roughness.

2.2.2. Symmetry-related domains. It may happen that on a surface many domains occur that are symmetry-related, *e.g.* an Si(100) surface that is (2 × 1) reconstructed will in general also have (1 × 2) domains (with normally the same occupancy). At 'fractional-order' positions, only one of the two domains contributes, but at integer-order positions one has to add the contributions of both. Rather than adding a second unit cell to the computation, it is more convenient to add the structure factor for the original unit cell, but computed for the corresponding symmetry-related Miller indices. This is performed by defining transformation matrices for the domains in the following way. Suppose the surface has N_d domains. The structure factor of domain n is given by:

$$F_{n,\mathbf{H}} = \sum_j \exp(2\pi i \mathbf{r}_{n,j} \cdot \mathbf{H}), \qquad (15)$$

where the atomic scattering factor and the Debye–Waller factor have been ignored for notational simplicity. Let matrix $\mathbf{A}_n$ transform the coordinates of the first unit cell into those of domain number n:

$$\mathbf{r}_{n,j} = \mathbf{A}_n \mathbf{r}_{1,j}. \qquad (16)$$

Then

$$F_{n,\mathbf{H}} = \sum_j \exp(2\pi i \mathbf{A}_n \mathbf{r}_{1,j} \cdot \mathbf{H}). \qquad (17)$$

Instead of transforming the real-space coordinates, we can arrive at the same structure factor by transforming the Miller indices, since

$$\mathbf{A}_n \mathbf{r}_{1,j} \cdot \mathbf{H} = \mathbf{r}_{1,j} \cdot \mathbf{A}_n^{-1}\mathbf{H} \equiv \mathbf{r}_{1,j} \cdot \mathbf{H}'_n, \ \text{with} \ \mathbf{H}'_n = \mathbf{A}_n^{-1}\mathbf{H}. \qquad (18)$$

In the summation over all domains in equation (9), one can thus use one unit cell, but calculating the corresponding $\mathbf{H}'_n$ for each domain. All the matrices $\mathbf{A}_n^{-1}$ need to be specified in *ROD* for this case.

3. Working with *ROD*

ROD uses a simple command-line interpreter for interactive work. Various menus and elementary help are available. More details are provided in the manual. The first version of *ROD* was written in C in 1989 and the program has been under constant modification since then. The first version was written for the MS-DOS operating system. Later, an OS/2 version was constructed, but as that operating system is hardly used anymore, nowadays the program is typically run as an MS-DOS session in a Windows95/98/NT environment. Since such a session has the full 640 Kbyte memory space available under standard MS-DOS, there are usually no severe memory problems. A version of *ROD* for the VMS operating system has been prepared, and other users have ported it to the UNIX environment (Vlieg, 1999). Nevertheless, the MS-DOS version is the most up to date one. There are plans to write a genuine Windows95/98/NT version.

For plotting graphs, the MS-DOS version of *ROD* uses the commercial package *GraphiC*™ (Scientific Endeavors Corporation, Kingston, TN, USA; e-mail: graphic@sciend.com; http://www.sciend.com). When using this version, the purchase of *GraphiC*™ is thus required.

Depending on the calculations one wants to perform, several input files are required. These are data file, surface-model file, bulk-model file, fit-model file and fit-parameter file. The format of these (ASCII) files is described in the manual. The files can be generated within *ROD*, by a text editor or by other programs. As an example, a surface-model file has the following format:
- First line: comments;
- Second line: the six lattice parameters;
- Other lines: element symbol plus fractional coordinates for each atom.

3.1. Structure refinement

Similar to bulk crystallography, surface-crystallography structure refinement involves comparison of calculated structure-factor amplitudes with measured ones. Several geometrical corrections need to be applied to the raw data before they can be converted to proper structure-factor amplitudes. These corrections depend on the experimental geometry and the surface diffractometer used (Vlieg, 1997, 1998).

In a structure analysis, the following parameters can be refined: scale factor; surface fraction; surface roughness; coordinates of the atoms in the surface unit cell; occupancy of the atoms in the surface unit cell; Debye–Waller parameters. In order to perform such a refinement, a fit model needs to be defined in *ROD* in which these fitting parameters are represented by a serial number. Because of symmetry constraints, when one atom is moved, often other atoms also need to be displaced in a symmetric fashion. Bulk-crystallography software often employs this symmetry information by using the corresponding space group. In that case only one atom from a symmetry-related set needs to be given by the user. This is not the case in the current version of *ROD*; all these relations have to be given by hand. Since surface unit cells are typically less complex than the bulk unit cells that are routinely solved nowadays, the need for this symmetry is less urgent for surface crystallography. The (plane group) symmetry is implemented in *ROD* using displacement parameters, as illustrated in Fig. 2 for a simple model in which three atoms have a common displacement parameter δ. The in-plane coordinates of these atoms are:

$$(1/3 + \delta, 1/3 + \delta), \quad (-1/3 - \delta, 0), \quad (0, -1/3 - \delta). \qquad (19)$$

In *ROD* the sign and magnitude of the displacement caused by each displacement parameter can be specified.

A structure refinement on the basis of a measured X-ray diffraction data set is normally performed by using a χ^2 minimization. The standard minimization procedure is the Levenberg-Marquardt method (Press *et al.*, 1988). When the theory varies strongly as a function of the fitted parameters or when it is difficult to find the global minimum, the method of simulated annealing is available. This is more robust, but slower than the Levenberg-Marquardt approach.

As an option, a Keating-energy minimization can be performed using the same structural model. The Keating model provides a simple description of the bulk elastic properties of covalent crystals
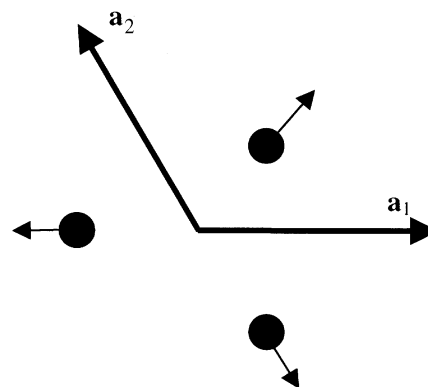

Figure 2
Top view of surface unit cell with lattice parameters $\mathbf{a}_1$ and $\mathbf{a}_2$ indicated and with three atoms that are displaced in a symmetric fashion.

(Keating, 1966; Pedersen, 1989). When the X-ray data set is not large or accurate enough to fit all independent parameters, one can try to fit some of the displacements using the Keating model. It is also possible to optimize the Keating energy and the X-ray fit simultaneously. In that case the weights of the two terms can be adjusted.

3.2. Other calculations

Before attempting a full refinement of a model, one typically starts by calculating structure factors of trial structures. *ROD* has various options for this; for example, a single rod can be calculated and plotted for a range of *l* values, or a range of structure factors can be calculated and plotted for a fixed *l* value (typically for in-plane data).

Fourier maps are also very important in deriving the correct structural model. *ROD* can generate Patterson maps, electron density maps and electron density difference maps. The symmetry-equivalent reflections necessary for this are automatically generated if the plane group is provided.

3.3. An example

ROD has been used in the past ten years to solve the structure of many surfaces and is at present used by several groups in several countries (Charlton *et al.*, 1997; Renaud, 1998; Edgar *et al.*, 1999). Here some of the possibilities of *ROD* are illustrated graphically for data on the Sb-induced $(3^{1/2} \times 3^{1/2})R30°$ reconstruction of Ag(111). For full details, see the publication by De Vries, Huisman *et al.* (1998). Fig. 3 shows a top view of the reciprocal space with the measured and calculated in-plane reflections depicted as half-circles. The radii of such circles are proportional to the structure-factor amplitude. From the fractional-order reflections (only very few in this example), the in-plane Patterson map can be computed (see Fig. 4). The Patterson function often yields important clues to deduce the relaxations present in the surface unit cell. Data and fit of a crystal truncation rod are shown in Fig. 5.

In addition to these graphs, it is possible to generate a multitude of alpha-numerical output (either to the computer screen or to a file) that can be used in the structure refinement.

4. Conclusions

ROD was not written with other users in mind, but several groups have found the program useful enough to employ it for their own surface crystallographic problems. For this reason the program and a manual are available upon request (Vlieg, 1999).

The technique of surface (and interface) diffraction is still under development, and consequently *ROD* is frequently being modified.
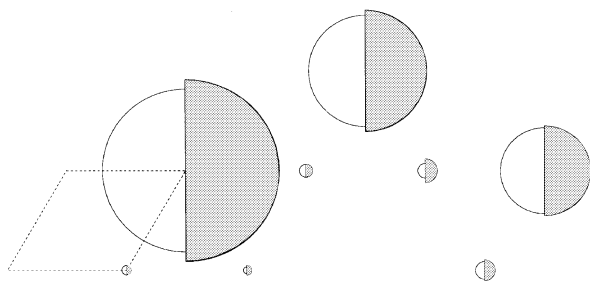
Figure 3
Top view of reciprocal space with the structure factors of in-plane reflections drawn as half-circles, each with a radius proportional to the amplitude. The left side of each circle represents the theory, the right side the data. The dashed diamond is the $(3^{1/2} \times 3^{1/2})R30°$ reciprocal unit cell.
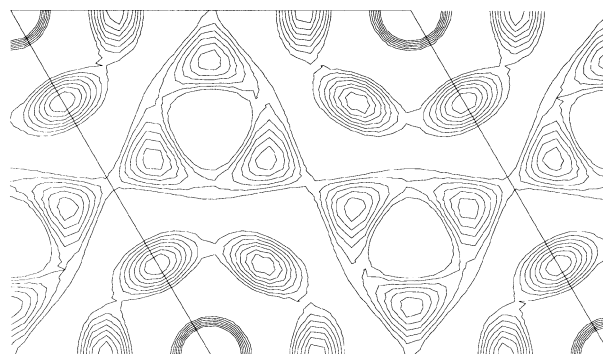
Figure 4
Top view of the surface unit cell, along with a depiction of the Patterson map from the fractional-order reflections. The diamond shows the $(3^{1/2} \times 3^{1/2})R30°$ unit cell.
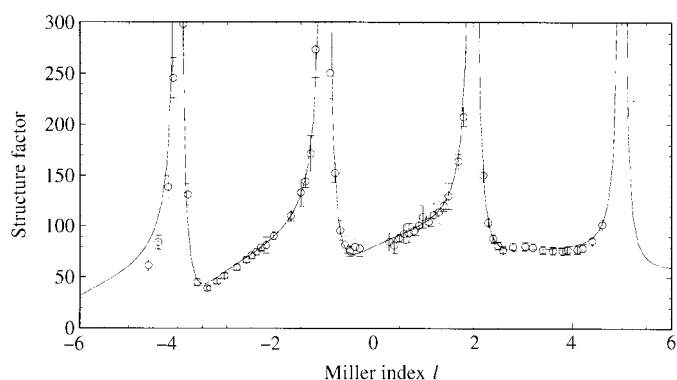
Figure 5
Structure-factor amplitudes $|F_{hkl}|$ of the (01) crystal truncation rods of Ag(111)–Sb as a function of perpendicular momentum transfer expressed in units of the Miller index *l*. Measured structure factors are indicated by filled circles. The solid curve represents calculations for the best-fit model (De Vries, Huisman *et al.*, 1998).

The present version, however, will fulfil most of the needs of a standard surface structure determination.

Since the first version of *ROD*, I have benefited from discussions with several colleagues, some of whom have also improved and/or contributed to the code. For this I want to thank in particular Ian Robinson, Paul Howes, Martin Lohmeier and Willem Jan Huisman. I thank Jelena Arsic and Marianne Reedijk for critically reading the manuscript.

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