A concise ROD manual

Elias Vlieg

RIM, Department of Solid State Chemistry, University of Nijmegen, Toernooiveld 1
6525 ED Nijmegen, The Netherlands. Email: vlieg@sci.kun.nl

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1 Basics

ROD is a program that can be used to do a refinement of a surface structure using surface X-ray diffraction data. It contains various options that were found to be useful in the past. Very likely, new options will be added if these are needed. ROD is thus a program that is frequently being modified. A general introduction to the technique of surface X-ray diffraction can be found in references [1-4]. A brief description of the program has been published [5]. Currently, a project is under way at the ESRF to make ROD available to a wide user community and on many platforms, while new features are added as well. More information can be found at the web site:


The program can be downloaded from that site as well.

In some sense, all ROD does is to calculate structure factors $F_{hkl}$:

$$F_{hkl} = \sum_j f_j e^{-B_j \sigma_j^2 / \lambda^2} e^{i2\pi(hx_i + ky_j + lz_j)} ,$$

(1)

with $f_j$ the atomic scattering factor of atom $j$, $B$ the Debye-Waller parameter, $(hkl)$ the diffraction 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’: (1) all atoms defined to be in the surface and (2) all atoms in the bulk, see fig. 1. The convention normally used in surface diffraction is that the lattice parameters $a_1$ and $a_2$ of the surface unit cell are lying in the surface plane and that $a_3$ is pointing outwards. Then the diffraction index $l$ is along the out-of-plane direction. The size of $a_3$ 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.

![Figure 1. Schematic of surface layer on top of a bulk crystal that extends to minus infinity. Unit cells for both sides are indicated.](image)

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

$$F_{\text{sum}} = F_{\text{surf}} + F_{\text{bulk}},$$

(2)

with
\[
F_{\text{surf}} = \sum_{j} f_{j} \Theta e^{-B_{j}Q^{2} \hat{q}^{2} \hat{\ell}^{2}} e^{2\pi i (h_{j} x_{j} + k_{j} y_{j} + l_{j} z_{j})},
\]
(3)

\[
F_{\text{bulk}} = \sum_{j=-\infty}^{0} f_{j} e^{2\pi i j \hat{a}_{x}} e^{i \alpha}
\]
(4)

and

\[
F_{u} = \sum_{j} f_{j} e^{-B_{j}Q^{2} \hat{q}^{2} \hat{\ell}^{2}} e^{2\pi i (h_{j} x_{j} + k_{j} y_{j} + l_{j} z_{j})}.
\]
(5)

In the definition of \( F_{\text{surf}} \) we included the occupancy parameter \( \Theta \), because in the surface unit cell not all positions need to be fully occupied. \( F_{\text{bulk}} \) describes the bulk unit cell structure factors \( F_{u} \) summed from the top layer to \(-\infty\). Because of the attenuation factor \( \alpha \), only a finite amount of unit cells contributes to \( F_{\text{bulk}} \). The summation (4) leads to:

\[
F_{\text{bulk}} = F_{u} \frac{1}{1 - e^{-2\pi i \hat{a}_{x} e^{-i \alpha}}}. \quad (6)
\]

\( F_{\text{bulk}} \) is the structure factor of a so-called crystal truncation rod (CTR). At integer values for \( l \) it has a very high intensity, but, due to the termination of the crystal at a sharp interface, even for non-integer \( l \) values there is a finite intensity.

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 increases the amount of layers in the surface unit cell from two to three. 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.

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 \( F_{\text{surf}} \). ROD has no problem calculating structure factors for fractional indices, but in general it is better to keep the in-plane diffraction indices integer by defining a larger unit cell. E.g. for a (2x1) reconstruction, \((n/2,m)\) reflections would occur in terms of the bulk unit cell with lattice parameters \( a_{1} \) and \( a_{2} \). Choosing as lattice parameters \( 2a_{1} \) and \( a_{2} \) leads to \((2n+1,m)\) reflections being exclusively coming from the surface, while \((2n,m)\) reflections are the interference sum of surface and bulk contributions. Only by choosing the larger lattice parameters, one uses 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.
2 More complicated situations

The simple situation described in the preceding section may not always represent reality. Things that may occur are:

1. the surface layer covers the bulk only partly
2. more than one type of surface layer is present (rarely occurs)
3. several symmetry-related surface unit cells are present
4. the crystal (bulk + surface) is rough.

All these situations can be dealt with, but a more complicated expression is necessary for $F_{\text{sum}}$. Figure 2 schematically shows how different parts of the crystal may be covered by different surface layers.

![Figure 2. A schematic top view of a crystal that is partially covered by two different surface unit cells.](image)

Define the following parameters:

- $S$: scale factor,
- $R$: roughness factor,
- $f_s$: fraction of crystal that is covered by surface layer,
- $f_{s2}$: fraction of $f_s$ that is covered by second type of surface layer (normally 0),
- $N_d$: total number of symmetry-related domains,
- $\alpha_j$: occupancy of domain $j$.

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

- $F_{b,j} = F_{b,j,\text{re}} + iF_{b,j,\text{im}}$: structure factor of $j$-th domain of the bulk
- $F_{s,j} = F_{s,j,\text{re}} + iF_{s,j,\text{im}}$: structure factor of $j$-th domain of first surface unit cell
- $F_{s2,j} = F_{s2,j,\text{re}} + iF_{s2,j,\text{im}}$: structure factor of $j$-th domain of second surface unit cell.

The important structure factors are now:
\[ F_{\text{bulk}} = SR \left[ \sum_{j} \alpha_j F_{b,j}^2 \right]^{\frac{1}{2}}, \]
\[ F_{\text{surf}} = SR \left[ f_s (1 - f_{s2}) \sum_{j} \alpha_j F_{s,j}^2 + f_s f_{s2} \sum_{j} \alpha_j F_{s2,j}^2 \right]^{\frac{1}{2}}, \]
\[ F_{\text{sum}} = SR \left[ (1 - f_s) \sum_{j} \alpha_j F_{b,j}^2 + f_s (1 - f_{s2}) \sum_{j} \alpha_j (F_{s,j} + F_{b,j})^2 + f_s f_{s2} \sum_{j} \alpha_j (F_{s2,j} + F_{b,j})^2 \right]^{\frac{1}{2}}. \] 

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 true that the various contributions need to be added coherently. In that case first the summation is performed and after that the result is squared:
\[ F_{\text{sum,coh}} = SR \left[ (1 - f_s) \sum_{j} \alpha_j F_{b,j}^2 + f_s (1 - f_{s2}) \left[ \sum_{j} \alpha_j (F_{s,j} + F_{b,j}) \right]^2 + f_s f_{s2} \left[ \sum_{j} \alpha_j (F_{s2,j} + F_{b,j}) \right]^2 \right]^{\frac{1}{2}}. \]

ROD allows choosing either of these situations.

2.1 Surface roughness

2.1.1 Approximate \( \beta \)-model

Various methods are available to include the effect of roughness. In general, surface roughness always leads to a decrease in scattered intensity. A very simple roughness model is the so-called \( \beta \)-model, in which surface level \( n \) has an occupancy \( \beta^n \), see figure 3.

![Figure 3. Surface roughness according to the so-called \( \beta \) model.](image)

For the simple cubic case illustrated in figure 3 and assuming that each layer consists of a complete unit cell it is straightforward to derive the roughness factor \( R \) by which the structure factor is reduced. For non-cubic crystals, or when also within a unit cell the occupancy varies from layer to layer, the calculation becomes more complicated. A formula that nevertheless is valid in many cases is:
\[ R = \frac{(1 - \beta)}{\left[(1 - \beta)^2 + 4\beta \sin^2 \frac{\pi (I - I_{Bragg})}{N_{layers}}\right]^{1/2}}, \]  

(11)

where \(I_{Bragg}\) is the \(l\)-value of the nearest Bragg peak and \(N_{layers}\) is the number of layers in the unit cell. Equation (11) works fine if \(N_{layers}\) denotes the number of equidistant layers within the unit cell. This situation is described within ROD as ‘approximated beta’. Different roughness distributions, or an exact calculation within the \(\beta\)-model, consume more computer time. It is therefore convenient to use equation (11) until proven otherwise.

2.1.2 Exact beta model

This model is intended as a test for the approximate beta model and works only for the bulk unit cell. The model is useful in order to illustrate the effect of the choice of \(N_{layers}\) on the structure factor, in particular when the layers are not equidistant or otherwise non-equivalent. It assumes that the last atom in the bulk unit cell has the lowest \(z\)-value (i.e., is the lowest atom). In the program, the contribution of the rough surface layers is stored in \(F_{surf}\), thus surface unit cells cannot be used simultaneously.

2.1.3 Numerical models

All the other available models calculate the occupancies numerically, and are thus somewhat slower. They 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 \(I_{Bragg}\) parameter. The atoms in the bulk unit cell need to be properly ordered, because the program determines the layer spacing vector \(R_{layer}\) from this and the value of \(N_{layer}\). The phase shift going from one layer to the next is: \(\psi_{hkl} = R_{layer}.H\). The total structure factor is then the sum over identical column structure factors \(F_{column}\) shifted by the appropriate phase factor and weighted by the occupancy \(q_n\):  
\[ F_{tot} = F_{column} \sum_n \theta_n e^{i\psi_{surf}}. \]

(12)

The reduction factor due to the roughness is now:  
\[ R = \left| \sum_n \theta_n e^{i\psi_{surf}} \right|^{1/2}. \]

(13)

Using this approach, we make errors in the absolute phase factors (but these are hardly used). The following roughness models are available:

1. beta model: same as before, different type of calculation
2. Poisson model: BETA represents the total coverage (\(\geq 0\)) in level distribution according to Poisson (random) statistics.
3. Gaussian: BETA is decay length (\(> 0\)) of Gaussian: \(e^{-n^2/\beta^2}\).
4. Linear: BETA is number of layers over which occupancy goes to zero (\(> 0\)).
5. Cosine: BETA is number of layers over which occupancy goes to zero over half the cycle of a cosine function.

6. Two-level: BETA is island coverage in simple two-level model (0 ≤ BETA < 1).

2.1.4 Fractional-order data

The models for surface roughness presented above are intended for integer-order data (CTR’s) and show a (strong) \( l \)-dependence. When there are no lateral correlations across steps, this \( l \)-dependence should be absent, as typically expected for fractional-order reflections. Each terrace will then contribute to the total intensity, not to the total amplitude (incoherent addition). There is still an effect of the roughness, but without \( l \)-dependence. If the coverage of level \( n \) is \( \theta_n \), then the total intensity for a fractional-order peak is:

\[
I_{\text{frac}}^{\text{rough}} = \sum_{n=0}^{m} (\theta_n - \theta_{n+1})^2.
\]  

(14)

For the beta model, with \( \theta_n = \beta^n \), this leads to:

\[
I_{\text{frac}}^{\text{rough}} = \frac{1-\beta}{1+\beta} \Rightarrow R = \sqrt{\frac{1-\beta}{1+\beta}}.
\]  

(15)

Fractional-order reflections for which the roughness needs to be calculated in this incoherent way, should be labeled with a non-integer value of \( l_{\text{Bragg}} \) (e.g. \( l_{\text{Bragg}} = 0.5 \)).

2.2 Symmetry-related domains

It may happen that on a surface many domains occur that are symmetry-related. E.g. a Si(100) surface that is (2x1) reconstructed will in general also have (1x2) domains (with normally the same occupancy). At ‘fractional-order’ positions, only one of the two domains contributes, but at CTR 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 diffraction indices. This is explained below.

Suppose the surface has \( N_d \) domains. The structure factor of domain \( n \) is given by (ignoring the atomic scattering factor and the Debye-Waller factor):

\[
F_{n,H} = \sum_j e^{2\pi i r_{n,j} \cdot \mathbf{H}},
\]  

(16)

Let matrix \( A_n \) transform the coordinates of the first unit cell into that of number \( n \):

\[
r_{n,j} = A_n r_{1,j}.
\]  

(17)

Then,

\[
F_{n,H} = \sum_j e^{2\pi i A_n r_{n,j} \cdot \mathbf{H}}.
\]  

(18)

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

\[
A_n r_{1,j} \cdot \mathbf{H} = r_{1,j} \cdot A_n^\dagger \mathbf{H} = r_{1,j} \cdot \mathbf{H}_n, \quad \text{with} \quad \mathbf{H}_n^\dagger = A_n^\dagger \mathbf{H}.
\]  

(19)
In the summation over all domains in equation (9) we can thus use one unit cell, but calculate the corresponding $H_n'$ for each domain.

### 2.3 Two scale factors

Ideally, measured structure factors are corrected in such a way that a single scale factor applies [5,6]. In practice, however, this ideal is not always reached. It is particularly difficult to obtain reflectivity data on the same scale as non-specular rods. Also, an insufficient detector acceptance and a difference in line width between integer-order and fractional-order data can cause a difference in scale factor between these two types of data. For this reason a second scale factor, SCALE2, can be used, depending on the value of $l_{\text{Bragg}}$. The scale factor used for a particular reflection is:

- If $l_{\text{Bragg}} < 0$: scale = SCALE*SCALE2;
- If $l_{\text{Bragg}} \geq 0$: scale = SCALE.

### 3 Working with ROD

#### 3.1 General

ROD uses a simple command-line interpreter for interactive work (the subroutines for this are in the file MENU.C). There are several menu’s available; when starting the program, one enters the main menu with prompt ROD>. Typing ‘help’ or ‘?’ produces a list of the available commands with a brief description. At least the part of each command shown in capital letters needs to be typed in, in order for the command-line interpreter to accept it. One may type as many commands on a single line as one likes. Execution starts after typing <Return>. If a mistake is made somewhere, the remainder of the command line is deleted. The command-line interpreter will only prompt for input if this is not given (or incorrectly given) in the command line. For starting users it is therefore convenient to type only one command at a time. The subsequently displayed prompt will usually explain what the required next step is.

When leaving the program (typing QUIT), the most important parameters are saved in a macro file ‘ROD_INIT.MAC’. Similarly the plot settings are saved in ‘PLOTINIT.MAC’. When restarting ROD, these two macro files are read in and most settings are therefore restored. These macro files simply consist of text lines that form valid command sequences in ROD. One can also generate separate macro files that can be executed using the command MACRO.

There are a few commands reserved for the command line interpreter itself. DEBUG will print the commands of a running macro file to the screen, NODEBUG will turn this option off. Similarly, TOFILEON/TOFILEOFF will start/stop writing all the output to a file with name menulist.txt.
The most up-to-date version of ROD runs under the MSDOS operating system (typically as a session in a Windows95/98/NT environment). Versions for the OS/2 and the VMS operating system have been made in the past, but are hardly used anymore. In collaboration with the ESRF, currently a version of ROD is being developed that will run on a number of platforms, including PC’s and UNIX workstations.

The plotting routines used in the MSDOS and OS/2 versions of ROD are from the commercial package GraphiC™. In order to make a plot, one only needs to use commands based on the command-line interpreter. Each platform has its own peculiarities. When making a plot in MSDOS, the screen will change from text mode to a screen-filling graphic mode. In this mode some options are available that can be displayed by typing e.g. an <a>. Typing <Return> will bring you back to text mode. Appendix A lists the available symbols and line styles in GraphiC™.

3.2 Input files

In order to do a structure analysis, one needs to be able to read in various types of files. These files can either be generated using a standard editor or be saved within ROD using the LIST command. The default output of LIST is the computer screen, but by specifying a file name, the output is written in the proper format to a file.

3.2.1 Data files

Data files (default extension .dat) have the following format:

```
first line comments
other lines:  h  k  l  f_data  sigma  [l_bragg]
```

It is thus a list of diffraction indices (hkl) followed by the structure factor and the standard error on the structure factor. \( l_{\text{Bragg}} \) values are optional and, if provided, are used in the following way:

- \( l_{\text{Bragg}} = \text{integer} \) : value of the nearest Bragg peak (used in approximate \( \beta \) model),
- \( l_{\text{Bragg}} < 0 \) : use second scale factor for associated reflection,
- \( l_{\text{Bragg}} = \text{non-integer} \) : apply incoherent roughness model (typical for fractional-order data).

Data files of this type and with properly estimated error bars can be generated from raw scan files by using e.g. the programs ANA and AVE. The data should normally consist of non-equivalent reflections. Converting measured integrated intensities to structure factors requires a whole range of correction factors, see refs. [6,7].
3.2.2 Surface model files

Surface model files (default extension .sur) allow one to read in the coordinates of a surface model. Format:

first line: comments
second line: \(a_1\ a_2\ a_3\ \alpha_{23}\ \alpha_{13}\ \alpha_{12}\) (lattice parameters)
other lines: element \(x\ y\ z\ [N_{DW}]\)

Each element is given its standard symbol, the \((x,y,z)\) position should be given in fractional coordinates. \(N_{DW}\) is the serial number for the Debye-Waller parameter for that atom (optional).

3.2.3 Bulk model files

Bulk model files (default extension .bul) allow one to read in the coordinates of the atoms in the bulk unit cell. The format is the same as for the surface model:

first line: comments
second line: \(a_1\ a_2\ a_3\ \alpha_{23}\ \alpha_{13}\ \alpha_{12}\) (lattice parameters)
other lines: element \(x\ y\ z\ [N_{DW}]\)

In order to calculate structure factors, at least one model (bulk or surface) has to be read in. If both are used, the lattice parameters have to be identical.

3.2.4 Fit model files

A surface model file contains fixed values for the coordinates of the atoms in the surface unit cell. When optimizing a surface structure, one needs to be able to change the positions of the atoms. Due to symmetry constraints, when one atom is moved, often also other atoms need to be displaced in a symmetric fashion. Bulk crystallography software often contains this symmetry information and only one atom from a symmetry-related set needs to be given by the user. This is not the case in ROD and all these relations have to be given by hand. This is done within ROD using displacement parameters. Figure 4 illustrates this for a simple model. Let \(\delta\) be the common displacement parameter of the three atoms. Then the in-plane coordinates of these atoms are:
Figure 4. Top view of surface unit cell with lattice parameters $a_1$ and $a_2$ and with three atoms that are displaced in a symmetric fashion.

\[(1/3+\delta,1/3+\delta)\]
\[(-1/3-\delta,0)\]
\[(0, -1/3-\delta).\]

The ingredients one needs to describe a position of an atom are therefore: starting position, displacement parameters and constants giving the direction and magnitude of the displacements. In order to be able to describe many situations, ROD has two sets of these parameters for each atom. The second set is only rarely needed and within the program this part is usually not shown (In ROD.SET.FIT> one has FULLMODEL NO). In a structure refinement one may want to optimize in addition: in-plane and out-of-plane Debye-Waller parameters and the occupancy.

All these parameters together are put in a fit file (default extension .fit), which has the following structure:

```
first line: comments
second line: $a_1$ $a_2$ $a_3$ $\alpha_{23}$ $\alpha_{13}$ $\alpha_{12}$ (lattice parameters)
other lines:
el $x_{\text{start}}$ $C_{x1}$ $N_\delta$ $C_{x2}$ $N_\delta$ $y_{\text{start}}$ $C_{y1}$ $N_\delta$ $C_{y2}$ $N_\delta$ $z_{\text{start}}$ $N_\delta$ $N_{\text{DW1}}$ $N_{\text{DW2}}$ $N_{\text{occ}}$
```

where $C$ are constants giving the magnitude of the displacement, $N_\delta$ are serial numbers of displacement parameters, $N_{\text{DW1}}$ is the serial number of the in-plane Debye-Waller parameter, $N_{\text{DW2}}$ is the serial number of the out-of-plane Debye-Waller parameter and $N_{\text{occ}}$ is the serial number of the occupancy parameter. Symmetry-related atoms are given the same $N_\delta$, $N_{\text{DW1}}$, $N_{\text{DW2}}$ and/or $N_{\text{occ}}$. When $N_{\text{DW2}} = 0$, the program uses the value of $N_{\text{DW1}}$ as an isotropic Debye-Waller parameter. When $N_{\text{occ}} = 0$, an occupancy of 1 is assumed. As an example, the $x$-value of atom $i$ is computed as:

$$x_i = x_{\text{start},i} + C_{x1,i} \cdot V(N_{\delta1,i}) + C_{x2,i} \cdot V(N_{\delta2,i}),$$

where $V(N_{\delta})$ is the value of the displacement parameter with serial number $N_{\delta}$. 
When performing a structure refinement, ROD optimizes the values of all variable parameters listed above (the ones with a serial number) and uses in addition an overall scale factor, the roughness parameter $\beta$ and the surface fraction $f_s$.

It is possible to generate/edit a fit file within ROD (in the ROD.SET.FIT> menu), but it is often more convenient to use a standard editor for this. When using a .fit file a .sur file is no longer needed, since the .fit file contains the same (and more) information. It is nevertheless often quicker to start with a .sur file, reading this into ROD and saving it as a .fit file using the list command (e.g., ROD>list fit test.fit). This will generate a template .fit file that can subsequently be edited.

In order to check whether a fit file has been correctly edited (with all the coupled displacements the file may become rather complicated), it is possible to make a very simple, in-plane projected plot of the surface unit cell. The parameters for this are set in ROD.SET.PLOT>, the actual plot is made in the ROD.PLOT> menu by using the commands MREFINED, MBOTH or MLARGE.

3.2.5 Fit parameter files

Fit parameter files (default extension .par) contain values of all fit parameters. They have the format of a macro file, i.e., all parameters are specified as a series of valid ROD command lines. When during a structure refinement a particularly nice fit is generated, the corresponding parameter values can be saved to a file by using the ROD>LIST PAR command.

3.3 Pre-set parameter values

In many calculations of rod, parameter values are used that can be preset in the ROD.SET> menu. Many are self-explanatory, but here we give a brief explanation of some of them.

3.3.1 Calculation parameters

These are the parameters that can be set in ROD.SET.CALC>. When calculating a rod profile, the range of $l$-values used is specified by: $l_{\text{start}}$, $l_{\text{end}}$ and $N_{\text{points}}$.

For special cases it is possible to use two different surface models. These are read in from one file (*.sur or *.fit). The second half of these files should contain the second model. The parameter $N_{\text{surf2}}$ tells how many atoms there are in the second model.

In order to avoid zero structure factors, start with a scale factor set at 1. The second scale factor is used when the parameter $l_{\text{Bragg}} < 0$.

The roughness parameter $\beta$ (discussed in section 2.1) is also set in this menu. In the sub-menu ROD.SET.CALC.ROUGH> a particular roughness model can be selected.
3.3.2 Fourier maps

A number of Fourier maps can be generated by ROD: Patterson map, electron density map and electron density difference map. In order to generate such a map, in principle all reflections, including symmetry-equivalent ones, are needed. By setting the appropriate plane group in ROD (ROD.SET.SYMMETRY>) these equivalent reflections will be automatically generated. The parameters needed for calculating the Fourier maps can be set in ROD.SET.PLOT>.

3.3.3 Symmetry-related domains

In ROD.SET.DOMAIN> the parameters needed to describe symmetry-related domains can be set. Depending on the unit cell chosen, one may either allow or disallow non-integer in-plane diffraction indices that are generated by the domain matrices to be included in the calculation. Normally all domains will be equally occupied. When the calculated structure factors are always zero, the origin is sometimes that the domain occupancy is accidentally set to zero.

3.4 Structure refinement

3.4.1 X-ray data

One normally refines a structure on the basis of a measured X-ray diffraction data set by using a $\chi^2$ minimization. The standard minimization procedure is the Levenberg-Marquardt method. When the theory varies very 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 Levenberg-Marquardt. These options are available in ROD.FIT>.

Several control parameters that determine how a fit is done, can be set in ROD.FIT.CONTROL>. In most cases the default parameters are sufficient. There are two ways in which errors are estimated for the fitting parameters. By default the covariance matrix is used [8]. This does take into account the correlation between parameters and derives an error corresponding to an increase in the non-normalized $\chi^2$ of 1. If the normalized $\chi^2$ value is larger than 1 (often the case!), the errors should (at least) be multiplied by the corresponding ratio. A second method to estimate the errors is to find the true increase in $\chi^2$ by doing full fits with all parameters free except the one for which the error is estimated (this is set by typing the command CHISQR in ROD.FIT.CONTROL>). This is repeated for all free parameters in a fit, and is thus much slower than the method using the covariance matrix. The desired increment in $\chi^2$ needs to be specified after the fit.

The results of a fit can be viewed in several ways. After an optimization cycle, the program will display the values of the fit parameters and the corresponding $\chi^2$-value. Using the command ROD>LIST COMPARE a list of experimental and calculated structure factors
is given, together with their $\chi^2$ differences. One can plot a calculated rod profile together with the data as a function of the diffraction index $l$ using ROD.PLOT>BOTH (there are also other ways). An in-plane data set can be plotted by using ROD.PLOT>FBOTH: this will draw the calculated (left-side) and experimental (right-side) structure factors as half-circles in the reciprocal plane.

### 3.4.2 Lattice energy

For complicated surface unit cells and/or small X-ray data sets, a structural refinement based on the X-ray data may not yield satisfactory results. It may happen, for example, that some bond lengths between atoms become smaller than expected chemically/physically. In ROD.ENERGY> it is possible to calculate and optimize the lattice energy of a structure model and thus to try to prevent unrealistic models. At the moment, two potentials are implemented: the Keating potential and the Lennard-Jones potential.

In 1966 Keating introduced a model for the elastic energy of a solid in order to describe the bulk elastic properties of covalent crystals. For models containing several kinds of atoms, the Keating elastic energy is [9]:

$$E = \alpha \sum_{\text{all bonds}} [r_{ij}^2 - (b_i + b_j)^2] + \beta \sum_{\text{all bond angles}} [r_{ij} \cdot r_{ik} - \cos(\alpha_{eqv}) (b_i + b_j)(b_i + b_k)]^2, \quad (21)$$

where $r_{ij}$ is the distance between atoms $i$ and $j$, $b_i$ is the (covalent) radius, $\alpha$ and $\beta$ are the parameters describing the energy cost of bond-length and bond-angle deformation, respectively, and $\alpha_{eqv}$ is the equilibrium bond angle. The Keating model is often used for tetrahedrally-bonded crystals for which $\cos(109.47^\circ)=-1/3$.

The Lennard-Jones potential between two equal atoms at separation $r$ is given by:

$$V_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]. \quad (22)$$

This potential has a value of $-\epsilon$ for $r = 1.122\sigma$. For our purpose, it is more convenient to have a value 0 at the equilibrium bond distance. For a structure with different atoms, we then obtain the following energy of the entire surface unit cell:

$$E_{LJ} = \sum_{\text{all bonds}} \alpha \left[ 1 + 4 \left( \frac{(b_i + b_j)}{1.122r_{ij}} \right)^{12} - \left( \frac{(b_i + b_j)}{1.122r_{ij}} \right)^6 \right], \quad (23)$$

where we have replaced the conventional $\epsilon$ in the potential by $\alpha$ in order to use the same parameter name as in the Keating energy.

Fig. 5 shows the difference between the two potentials. If the lattice energy is used to prevent too short bond distances, the Lennard-Jones is most appropriate, because it only has a mild energy penalty for too long bonds. Even though the real potential in a system may be neither of the Keating or the Lennard-Jones type, the two can nevertheless be used as a penalty function during a fit.
Fig. 5. The difference in the Keating and (modified) Lennard-Jones potential for an equilibrium bond distance of 3 Å and $\alpha = 0.2$ for Keating and $\epsilon (= \alpha) = 1$ for Lennard-Jones.

In ROD.ENERGY> a lattice-energy minimization can be performed using either of these potentials. First the potential has to be chosen and values have to be given for the corresponding parameters: $\alpha$, $\beta$, $b_i$ and $\alpha_{equ}$ for Keating and $\alpha (= \epsilon)$ and $b_i$ for Lennard-Jones. Second, all atoms participating in the lattice-energy calculation need to be specified (not all have to be included). The program can then automatically find all bonds and angles in the surface unit cell that are smaller than 110\% of the equilibrium values (command FINDBONDS). Bonds that should not be included (e.g. because the parameters for such bonds are not known) can subsequently be removed. Please note that the bond-searching algorithm ignores (for simplicity reasons) bonds of an atom to itself on an equivalent position (in a neighboring unit cell). This means that the lattice energy may fail for small 1x1 unit cells.

In a lattice-energy minimization a refinement is done using the same displacement parameters as are used in fitting X-ray data. In practice, when the X-ray data set is not large enough to fit all independent parameters, one may e.g. want to fit the large, top-most displacements using the X-ray data and estimate the smaller, deeper displacements from the lattice-energy model. When the Keating energy is used for non-covalent crystals, the bond-angle term may be ignored by putting the parameter $\beta$ to zero (or by setting $\alpha_{equ}$ to such a small value that no angles will be included in the calculation).

When separating the lattice-energy minimization from the X-ray fit, one typically performs a number of iterations between an X-ray and a lattice-energy refinement. It is also possible to include the lattice-energy in the $\chi^2$ minimization of the X-ray data and thus to optimize these two terms simultaneously. This option is switched on by setting the ‘chisqr’ flag in ROD.ENERGY>. This will simply add the lattice energy (in eV’s!) to the (non-normalized) $\chi^2$ value. The relative weight between the energy term and the X-ray $\chi^2$-term can
be adjusted by changing the values of $\alpha$ and $\beta$. The addition of the lattice energy to the total $\chi^2$ is done using a trick that may lead to errors if the minimization fails (due to mathematical exceptions or an abort). In that case the data should be read in again.

Acknowledgements
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4 References
Appendix A. GraphiC™ information

Below the available line styles and symbols are shown.

1. ________________________________
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Appendix B. Examples of input files

Below are listed examples of valid input files. The example is from the Ag(111)-(√3x√3)R30°-Sb surface. For details about this particular reconstruction, see S.A. de Vries, W.J. Huisman, P. Goedtkindt, M.J. Zwanenburg, S.L. Bennett, I.K. Robinson and E. Vlieg, Surface Sci. 414 (1998) 159.

A bulk model file (*.bul).
Ag(111) bulk unit cell in root3 frame:
5.0039 5.0039 7.0766 90 90 120
Ag 0.00000 0.00000 0.00000 1
Ag 0.66667 0.33333 0.00000 1
Ag 0.33333 0.66667 0.00000 1
Ag 0.33333 0.33333 -0.33333 1
Ag 0.66667 0.00000 -0.33333 1
Ag 0.00000 0.66667 -0.33333 1
Ag 0.33333 0.00000 -0.66667 1
Ag 0.66667 0.66667 -0.66667 1
Ag 0.00000 0.33333 -0.66667 1

A surface model file (*.sur)
Sb/Ag(111) surface cell in root3 frame:
5.0039 5.0039 7.0766 90 90 120
Sb 0.33333 0.33333 1.33333 1
Ag 0.66667 0.00000 1.33333 1
Ag 0.00000 0.66667 1.33333 1
Ag 0.00000 0.00000 1.00000 1
Ag 0.66667 0.33333 1.00000 1
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Ag 0.33333 0.00000 0.33333 1
Ag 0.66667 0.66667 0.33333 1
Ag 0.00000 0.33333 0.33333 1

A fit model file (*.fit)
5.0039 5.0039 7.0766 90.000 90.000 120.000
Sb 0.33333 1.0000 0.0000 0.33333 1.0000 0.0000 0.0000 0.0000 0.33333 2 1 0 0
Ag 0.66667 1.0000 0.0000 0.0000 1.0000 0.0000 0.0000 0.0000 1.33333 3 1 0 0
Ag 0.00000 1.0000 1.0000 0.0000 0.0000 1.0000 0.0000 0.0000 1.33333 3 1 0 0
Ag 0.00000 1.0000 0.0000 0.0000 1.0000 0.0000 0.0000 0.0000 1.0000 0 1 0 0
Ag 0.66667 -1.0000 1.0000 0.0000 0.33333 0.0000 1.0000 0.0000 1.0000 0 1 0 0
Ag 0.33333 0.0000 0.0000 0.66667 -1.0000 1.0000 0.0000 0.0000 1.0000 0 1 0 0
Ag 0.33333 1.0000 0.0000 0.0000 0.33333 1.0000 0.0000 0.0000 0.66667 0 1 0 0
Ag 0.66667 1.0000 0.0000 0.0000 0.0000 1.0000 0.0000 0.0000 0.66667 0 1 0 0
Ag 0.00000 1.0000 0.0000 0.0000 0.66667 1.0000 0.0000 0.0000 0.66667 0 1 0 0
Ag 0.33333 1.0000 0.0000 0.0000 0.0000 1.0000 0.0000 0.0000 0.33333 0 1 0 0
Ag 0.66667 1.0000 0.0000 0.0000 0.66667 1.0000 0.0000 0.0000 0.33333 0 1 0 0
Ag 0.00000 1.0000 0.0000 0.0000 0.33333 1.0000 0.0000 0.0000 0.33333 0 1 0 0
A parameter file (*.par)
!best-fit parameter values for Ag(lll)-sqrt3-Sb
!Goto set parameter menu
set par
scale         0.6821    0.0500    2.0000  YES
beta          0.0000    0.0000    0.5000  YES
surffrac      0.7546    0.5000    1.0000  YES
displace 1   0.0122   -0.2000    0.2000  YES
displace 2   0.0238   -0.2000    0.2000  YES
displace 3   0.0193   -0.2000    0.2000  YES
bl 1        0.6600    0.0000    0.0000  NO
return return

Part of a data file (*.dat)
Ag(lll)-sqrt3xsqrt3-Sb data first run
1  0   0.200    3.67    0.42     0
1  0   0.400    3.04    0.51     0
1  0   0.600    3.42    0.53     0
1  0   0.800    3.65    0.60     0
1  0   1.005    3.25    0.62     0
1  0   1.200    3.19    0.68     0
1  0   1.400    2.13    0.91     0
1  0   1.600    1.00    5.00     0
1  0   1.800    1.00    5.00     0
1  0   2.005    6.18    0.85     0
1  0   2.200    5.30    0.89     0
1  0   2.400    5.52    0.91     0
1  0   2.600    4.14    1.02     0
1  1   -2.600   64.13    6.42     2
1  1   -2.500   69.08    6.92     2
1  1   -2.300   77.81    7.79     2
1  1   -2.200   81.48    8.16     2
1  1   -2.050   90.52    9.06     2
1  1   -1.700  114.09   11.41     2
1  1   -1.500  133.15   13.32     2
1  1   -1.400  157.08   15.71     2
1  1   -1.300  171.53   17.16     2
1  1   -1.200  273.63   27.37     2
1  1   -0.900  250.59   25.06     2
1  1   -0.800  149.52   14.96     2
1  1   -0.700  96.07     9.62     2
1  1   -0.600  82.07     8.21     2
1  1   -0.500  75.89     7.60     2
1  1   -0.400  80.05     8.01     2
1  1   -0.300  78.38     7.85     2
1  1   -0.200  92.03     9.21     2
1  1   -0.200  87.75     8.78     2
1  1   -0.300  84.85     8.49     2
1  1   -0.400  81.40     8.15     2
1  1   -0.500  87.63     8.77     2
1  1   -0.600  92.58     9.26     2
1  1   -0.700  93.41     9.34     2
1  1   -0.800  94.27     9.43     2
1  1   -0.900 101.10    10.11     2
1  1   -0.980 109.64    10.97     2
1  1   -1.100 106.93    10.70     2
1  1   -1.200 111.40    11.14     2
Appendix C. List of all commands

*********************************************************************** MAIN MENU ***********************************************************************
Read : Read data/model files
List : List data/model
RESet : Reset all parameters
Calculate : Calculate structure factors
Plot : Goto plotting menu
Set : Set parameters
Fit : Fit experimental structure factors
Energy : Goto lattice energy menu
Macro : Run macro file
: : Execute an operating system command
Help : Display menu
QUIT : Quit program

*********************************************************************** LIST MENU ***********************************************************************
Bulk : Bulk contribution
SURface : Surface contribution
Sum : Interference sum of bulk and surface
All : Above three values
Data : Structure factor data
SModel : Surface model
BModel : Bulk model
Fit : Fitting model for surface structure
Compare : Comparison between data and theory
Parameters : Values of fit parameters
Symmetry : Symmetry-equivalent reflections of data
Bonds : Bond lengths of surface structure
Help : Display menu
Return : Return to main menu

*********************************************************************** CALCULATION MENU ***********************************************************************
Rod : Calculate rod profile
Range : Calculate f's for range of h and k
Qrange : Calculate f's within q-max
Data : Calculate f's for all data points
Distance : Calculate the distance between two atoms
Angle : Calculate bond angle between three atoms
LEffective : Calculate effective l from slit width
ROUGHness : Calculate roughness in atomic layers
Help : Display menu
Return : Return to main menu

*********************************************************************** PLOT MENU ***********************************************************************
Bulk : Bulk contribution (against l)
SURface : Surface contribution (against l)
Sum : Interference sum of bulk and surface
All : Above three curves (against l)
Data : Rod data (against l)
Both : Data plus calculated interference sum
FTheory : Theoretical structure factors
FData : Experimental structure factors
FBoth : Theoretical and experimental f’s
MOriginal : Original structure model
MRefined : Refined structure model
MBoth : Original + refined structure model
MLarge : Several unit cells of refined model
M3d : Refined model, PLOT3D output file
Cut : Cut trough scattering plane, PLOT3D
MSI : Refined model, MSI output file
DPatterson : Patterson function of experimental data
TPatterson : Patterson of theoretical structure f’s
Difference : Electron density difference map
Electron : Electron density map of model
Errors : Set error bar plotting on/off
Unit : Set drawing of unit cell on/off
Help : Display menu
Return : Return to main menu

*********************************************************************** SET MENU ***********************************************************************
Calculate : Parameters for rod calculation
Fit : Model par. for fitting surface structure
Parameters : Values of fit parameters
Domain : Parameters describing the domains
Equal : All domains equal occupancy yes/no
Occupancy : Set occupancy parameters of domain n
Coherent : Add rotational domains coherently yes/no
List : List parameters
Help : Display menu
Return : Return to main menu

ROD.SET.DOMAIN>
********************************** SET PLOT PARAMETERS **********************************
Size : Size of circles in plot of f's
Threshold : Plotting threshold for f's
Radius : Radius of atom in plot of model
XMIncont : Lower bound on x value in Patterson
XMMaxcont : Upper bound on x value in Patterson
YMIncont : Lower bound on y value in Patterson
YMMaxcont : Upper bound on y value in Patterson
NXcontour : Number of steps along x in Patterson
NYcontour : Number of steps along y in Patterson
MInlevel : Minimum contour level in Patterson
MAxlevel : Maximum contour level in Patterson
Nlevel : Number of contour levels in Patterson
List : List parameters
Help : Display menu
Return : Return to main menu

ROD.SET.PLOT>
********************************** SET PLANE GROUP SYMMETRY **********************************
P1 : Plane group no. 1
P2 : Plane group no. 2
PM : Plane group no. 3
PG : Plane group no. 4
CM : Plane group no. 5
P2MM : Plane group no. 6
P2MG : Plane group no. 7
P2GG : Plane group no. 8
C2MM : Plane group no. 9
P4 : Plane group no. 10
P4MM : Plane group no. 11
P4GM : Plane group no. 12
P3 : Plane group no. 13
P3M1 : Plane group no. 14
P31M : Plane group no. 15
P6 : Plane group no. 16
P6MM : Plane group no. 17
List : List current plane group
Help : Display menu
Return : Return to main menu

ROD.SET.SYMMETRY>
********************************** SET FITTING PARAMETERS **********************************
Value : Set parameter value
LOWER : Set lower parameter limit
Upper : Set upper parameter limit
CHECK : Toggle range checking
Fix : Fix a parameter value
Loose : Make parameter free
Center : Center parameter within range
Fall : Fix all parameters
ALL : Make all parameters free
ALL : Center all parameters
Control : Set control parameters
List : List parameter values
Help : Display menu
Run : Start fit (Levenberg Marquardt)
Cool : Start fit (cool down algorithm)
Asa : Start fit (adaptive sim. ann.)
Return : Return without fitting

ROD.FIT>
********************************** SET CONTROL PARAMETERS **********************************
Covariance: Use covariance matrix for error estimate
Chisqr : Use chi^2 for error estimate
ITermax : Max. number of iterations (LM fit)
NSteps : Number of steps per temperature
NLList : Number of steps between lists
NDecade : # of anneals per temp. decade
Tstart : Initial temperature
MaxSets : Maximum number of parameter sets
Mult : Multiplier for step computation
Conv : chi^2 convergence criterion
MINTemps : Minimum number of converging anneals

Return : Return without fitting
MINSteps : Minimum number of steps per set
Threshold : Threshold for generation of new set
Pairing : Threshold for pairing of two sets
Credit : Credit for new parameters set
Decrement : Credit decrement per step
Log : Use logarithm of data
File : Specify log file for fitting
List : List parameters
Help : This list
Return : Return to main menu

***************************** LATTICE ENERGY MENU ****************************
Alpha : Set bond length deformation par.
Beta : Set bond angle deformation par.
Radius : Set atomic radius
Equangle : Set equilibrium bond angle
Keating : Use Keating potential
Lennard : Use Lennard-Jones potential
Include : Include atom in Keating calculation
Exclude : Exclude atom in Keating calculation
Remove : Remove a bond from calculation
Findbonds : Find all bonds between atoms
Chisqr : Include energy in chi^2 minimization
Energy : Calculate lattice energy
Minimize : Minimize lattice energy
List : List parameter values
Bondlist : List bonds between atoms
Anglelist : List angles between atoms
Help : Display menu
Return : Return to main menu

ROD.ENERGY>