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A concise ROD manual

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1 Basics 2
2 More complicated situations 4
  2.1 Surface roughness 5
    2.1.1 Approximate β-model 5
    2.1.2 Exact beta model 6
    2.1.3 Numerical models 6
    2.1.4 Fractional-order data 7
  2.2 Symmetry-related domains 7
  2.3 Two scale factors 8
3 Working with ROD 8
  3.1 General 8
  3.2 Input files 9
    3.2.1 Data files 9
    3.2.2 Surface model files 10
    3.2.3 Bulk model files 10
    3.2.4 Fit model files 10
    3.2.5 Fit parameter files 12
  3.3 Pre-set parameter values 12
    3.3.1 Calculation parameters 12
    3.3.2 Fourier maps 13
    3.3.3 Symmetry-related domains 13
  3.4 Structure refinement 13
    3.4.1 X-ray data 13
    3.4.2 Lattice energy 14
4 References 16
Appendix A. GraphiC™ information 17
Appendix B. Examples of input files 18
Appendix C. List of all commands 20

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:

www.esrf.fr/computing/scientific/joint_projects/ANA-ROD/index.html

The program can be downloaded from that site as well.

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

$$F_{hkl} = \sum_j f_j e^{-B_j Q^2/(16p^2)} e^{2pi(hx_j+ky_j+lz_j)} , \qquad (1)$$

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 $\mathbf{a}_1$ and $\mathbf{a}_2$ of the surface unit cell are lying in the surface plane and that $\mathbf{a}_3$ is pointing outwards. Then the diffraction 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.

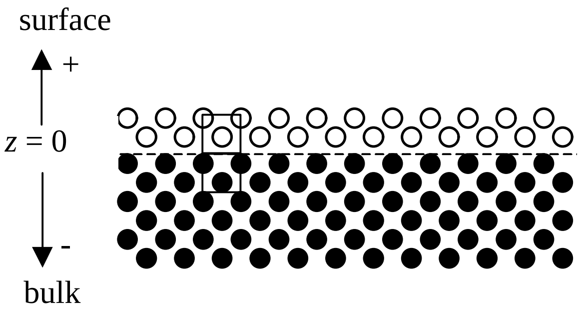

Figure 1. Schematic of surface layer on top of a bulk crystal that extends to minus infinity. Unit cells for both sides are indicated.

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

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

with

$$F_{surf} = \sum_{j}^{\substack{surface\\ unit\,cell}} f_j q_j e^{-B_j Q^2/(16p^2)} e^{2pi(hx_j+ky_j+lz_j)} , \tag{3}$$

$$F_{bulk} = \sum_{j=-\infty}^{0} F_u e^{2pilj} e^{ja} \tag{4}$$

and

$$F_u = \sum_{j}^{\substack{bulk\\ unit\,cell}} f_j e^{-B_j Q^2/(16p^2)} e^{2pi(hx_j+ky_j+lz_j)} . \tag{5}$$

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

$$F_{bulk} = F_u \frac{1}{1-e^{-2pil}e^{-a}} . \tag{6}$$

F_{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_{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 $\mathbf{a}_1$ and $\mathbf{a}_2$. Choosing as lattice parameters 2$\mathbf{a}_1$ and $\mathbf{a}_2$ 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_{sum}. Figure 2 schematically shows how different parts of the crystal may be covered by different surface layers.

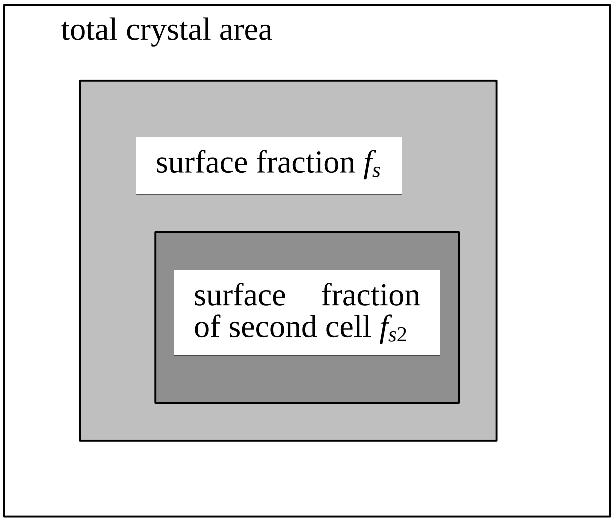

Figure 2. A schematic top view of a crystal that is partially covered by two different surface unit cells.

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,
a_j	occupancy of domain j.

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

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

The important structure factors are now:

$$F_{bulk} = SR\left[\sum_j a_j F_{b,j}^2\right]^{1/2}, \tag{7}$$

$$F_{surf} = SR\left[f_s(1-f_{s2})\sum_j a_j F_{s,j}^2 + f_s f_{s2}\sum_j a_j F_{s2,j}^2\right]^{1/2}, \tag{8}$$

$$F_{sum} = SR\left[(1-f_s)\sum_j a_j F_{b,j}^2 + f_s(1-f_{s2})\sum_j a_j (F_{s,j}+F_{b,j})^2 + f_s f_{s2}\sum_j a_j (F_{s2,j}+F_{b,j})^2\right]^{1/2}. \tag{9}$$

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 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:

$$F_{sum,coh} = SR\left\{(1-f_s)\left[\sum_j a_j F_{b,j}\right]^2 + f_s(1-f_{s2})\left[\sum_j a_j (F_{s,j}+F_{b,j})\right]^2 + f_s f_{s2}\left[\sum_j a_j (F_{s2,j}+F_{b,j})\right]^2\right\}^{1/2} \tag{10}$$

ROD allows choosing either of these situations.

2.1 *Surface roughness*

2.1.1 Approximate β-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 *b*-model, in which surface level *n* has an occupancy b^n, see figure 3.

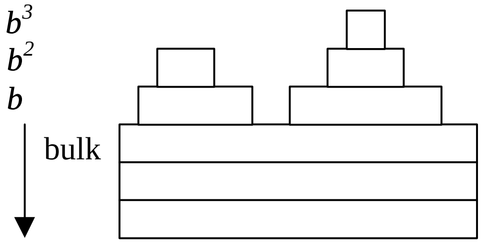

Figure 3. Surface roughness according to the so-called *b* model.

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:

$$R = \frac{(1-b)}{\left[(1-b)^2 + 4b\sin^2\frac{p(l-l_{Bragg})}{N_{layers}}\right]^{1/2}}, \tag{11}$$

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 (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 b-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 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 and the value of N_{layer}. The phase shift going from one layer to the next is: $y_{hkl} = \mathbf{R}_{layer} \cdot \mathbf{H}$. The total structure factor is then the sum over identical column structure factors F_{column} shifted by the appropriate phase factor and weighted by the occupancy q_n:

$$F_{tot} = F_{column} \sum_n q_n e^{iny_{hkl}}\ . \tag{12}$$

The reduction factor due to the roughness is now:

$$R = \left| \sum_n q_n e^{iny_{hkl}} \right|^{1/2}. \tag{13}$$

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 (≥ 0) in level distribution according to Poisson (random) statistics.
3. Gaussian: BETA is decay length (> 0) of Gaussian: e^{-n^2/b^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 ($0 \le \text{BETA} < 1$).

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 q_n, then the total intensity for a fractional-order peak is:

$$I_{fract}^{rough} = \sum_{n=0}^{\infty} (q_n - q_{n+1})^2 . \tag{14}$$

For the beta model, with $q_n = b^n$, this leads to:

$$I_{fract}^{rough} = \frac{1-b}{1+b} \Rightarrow R = \sqrt{\frac{1-b}{1+b}} . \tag{15}$$

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_{Bragg} (e.g. $l_{Bragg} = 0.5$).

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):

$$F_{n,\mathbf{H}} = \sum_j e^{2pi\mathbf{r}_{n,j}\cdot\mathbf{H}} , \tag{16}$$

Let matrix $\mathbf{A}_n$ transform the coordinates of the first unit cell into that of number *n*:

$$\mathbf{r}_{n,j} = \mathbf{A}_n\, \mathbf{r}_{1,j}. \tag{17}$$

Then,

$$F_{n,\mathbf{H}} = \sum_j e^{2pi\mathbf{A}_n\mathbf{r}_{1,j}\cdot\mathbf{H}} . \tag{18}$$

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

$$\mathbf{A}_n\mathbf{r}_{1,j} \cdot \mathbf{H} = \mathbf{r}_{1,j} \cdot \mathbf{A}_n^{-1}\mathbf{H} \equiv \mathbf{r}_{1,j} \cdot \mathbf{H}_n^{'}, \text{ with } \mathbf{H}_n^{'} = \mathbf{A}_n^{-1}\mathbf{H} . \tag{19}$$

In the summation over all domains in equation (9) we can thus use one unit cell, but calculate the corresponding $\mathbf{H}_n'$ 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_{Bragg}. The scale factor used for a particular reflection is:

If $l_{Bragg} < 0$: scale = SCALE*SCALE2;
If $l_{Bragg} \geq 0$: 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 [lbragg]`

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

l_{Bragg} = integer : value of the nearest Bragg peak (used in approximate *b* model),
$l_{Bragg} < 0$: use second scale factor for associated reflection,
l_{Bragg} = 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:	$\mathbf{a}_1$	$\mathbf{a}_2$	$\mathbf{a}_3$	α_{23}	α_{13}	α_{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:	$\mathbf{a}_1$	$\mathbf{a}_2$	$\mathbf{a}_3$	α_{23}	α_{13}	α_{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 d be the common displacement parameter of the three atoms. Then the in-plane coordinates of these atoms are:

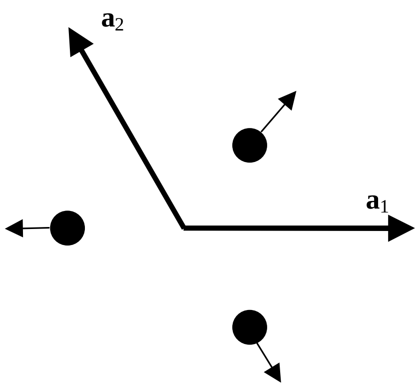

Figure 4. Top view of surface unit cell with lattice parameters $\mathbf{a}_1$ and $\mathbf{a}_2$ and with three atoms that are displaced in a symmetric fashion.

$(1/3+d,1/3+d)$
$(-1/3-d,0)$
$(0, -1/3-d)$.

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: $\mathbf{a}_1$ $\mathbf{a}_2$ $\mathbf{a}_3$ α_{23} α_{13} α_{12} (lattice parameters)
other lines:
`el` x_{start} C_{x1} N_d C_{x2} N_d y_{start} C_{y1} N_d C_{y2} N_d z_{start} N_d N_{DW1} N_{DW2} N_{occ}

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

$$x_i = x_{start,i} + C_{x1,i} * V(N_{d1,i}) + C_{x2,i} * V(N_{d2,i}), \tag{20}$$

where $V(N_d)$ is the value of the displacement parameter with serial number N_d.

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 ***b*** 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_{start}, l_{end} and N_{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_{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 $l_{Bragg} < 0$.

The roughness parameter ***b*** (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 c^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* c^2 of 1. If the *normalized* c^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 c^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 c^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 c^2-value. Using the command ROD>LIST COMPARE a list of experimental and calculated structure factors is given, together with their c^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]:

$$E = a \sum_{\substack{all \\ bonds}} \left[r_{ij}^2 - (b_i + b_j)^2 \right]^2 + b \sum_{\substack{all\,bond \\ angles}} \left[\mathbf{r}_{ij} \cdot \mathbf{r}_{ik} - \cos(a_{equ})(b_i + b_j)(b_i + b_k) \right]^2 , \tag{21}$$

where r_{ij} is the distance between atoms i and j, b_i is the (covalent) radius, a and b are the parameters describing the energy cost of bond-length and bond-angle deformation, respectively, and a_{equ} is the equilibrium bond angle. The Keating model is often used for tetrahedrally-bonded crystals for which cos(109.47°)=-1/3.

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

$$V_{LJ} = 4e \left[\left(\frac{s}{r} \right)^{12} - \left(\frac{s}{r} \right)^{6} \right]. \tag{22}$$

This potential has a value of $-e$ for $r = 1.122s$. 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:

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

where we have replaced the conventional e in the potential by a 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.

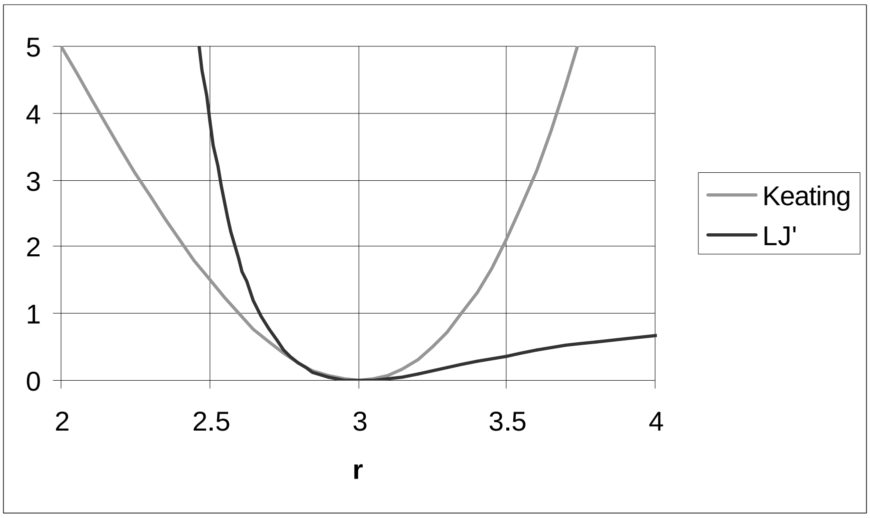

Fig. 5. The difference in the Keating and (modified) Lennard-Jones potential for an equilibrium bond distance of 3 Å and a = 0.2 for Keating and e (= a) = 1 for Lennard-Jones.

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: a, b, b_i and α_{equ} for Keating and a (= e) 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 b to zero (or by setting α_{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 c^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) c^2 value. The relative weight between the energy term and the X-ray c^2-term can be adjusted by changing the values of α and β. The addition of the lattice energy to the total c^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

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, Willem Jan Huisman, Odile Robach, Detlef Smilgies en Olof Svensson.

4 References

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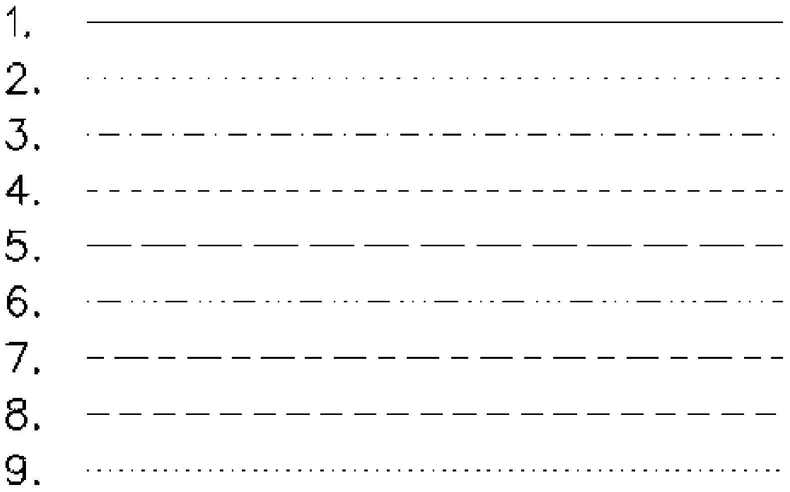
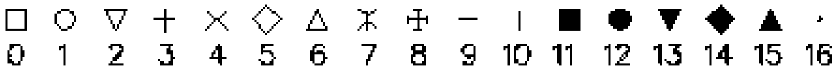
Appendix A. GraphiCä information

Below the available line styles and symbols are shown.





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
Ag      0.33333 0.66667  1.00000 1
Ag      0.33333 0.33333  0.66667 1
Ag      0.66667 0.00000  0.66667 1
Ag      0.00000 0.66667  0.66667 1
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  0.0000  0  0.33333  1.0000  0  0.0000  0  1.33333 2 1 0 0
Ag  0.66667  1.0000  0  0.0000  0  0.00000  1.0000  0  0.0000  0  1.33333 3 1 0 0
Ag  0.00000  1.0000  0  0.0000  0  0.66667  1.0000  0  0.0000  0  1.33333 3 1 0 0
Ag  0.00000  1.0000  1  0.0000  0  0.00000  1.0000  1  0.0000  0  1.00000 0 1 0 0
Ag  0.66667 -1.0000  1  0.0000  0  0.33333  0.0000  1  0.0000  0  1.00000 0 1 0 0
Ag  0.33333  0.0000  1  0.0000  0  0.66667 -1.0000  1  0.0000  0  1.00000 0 1 0 0
Ag  0.33333  1.0000  0  0.0000  0  0.33333  1.0000  0  0.0000  0  0.66667 0 1 0 0
Ag  0.66667  1.0000  0  0.0000  0  0.00000  1.0000  0  0.0000  0  0.66667 0 1 0 0
Ag  0.00000  1.0000  0  0.0000  0  0.66667  1.0000  0  0.0000  0  0.66667 0 1 0 0
Ag  0.33333  1.0000  0  0.0000  0  0.00000  1.0000  0  0.0000  0  0.33333 0 1 0 0
Ag  0.66667  1.0000  0  0.0000  0  0.66667  1.0000  0  0.0000  0  0.33333 0 1 0 0
Ag  0.00000  1.0000  0  0.0000  0  0.33333  1.0000  0  0.0000  0  0.33333 0 1 0 0
```

A parameter file (*.par)

```
!best-fit parameter values for Ag(111)-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
b1        1   0.6600    0.0000    0.0000  NO
return return
```

Part of a data file (*.dat)

```
Ag(111)-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        5         0
   1    0   1.800     1        5         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  -2.400    72.67     7.28      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
ROD>
********************************** 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
ROD.LIST>
******************************* 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
ROD.CALC>
********************************** 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
 CUt3d     : 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
ROD.PLOT>
*********************************** SET MENU **********************************
 Calculate : Parameters for rod calculation
 Fit       : Model par. for fitting surface structure
 PArameters: Values of fit parameters
 Domain    : Parameters describing the domains
```

```
 Plot      : Plotting parameters
 SYmmetry  : Plane group symmetry of model
 Help      : Display menu
 Return    : Return to main menu
ROD.SET>
************************ SET ROD CALCULATION PARAMETERS ***********************
 STructure : Use structure factors or intensities
 LStart    : Start value of l
 LEnd      : End value of l
 Npoints   : Number of points on rod
 Atten     : Attenuation factor of beam
 Beta      : Roughness parameter beta
 LBragg    : l-value of nearest Bragg peak
 NLayers   : Number of layers in bulk unit cell
 SCale     : Scale factor of theory
 SCALE2    : 2nd scale factor of theory
 SFraction : Fraction of surface with 1st unit cell
 S2fraction: Fraction of surface with 2nd unit cell
 NSurf2    : Number of atoms in 2nd unit cell
 ROUghness : (Temporary) roughness mode calculation
 List      : List parameters
 Help      : Display menu
 Return    : Return to main menu
ROD.SET.CALC>
****************************** SET ROUGHNESS MODE *****************************
 Approx    : Approximated beta model
 Exact     : Exact beta model (BULK ONLY!)
 Beta      : Numerical beta model
 Poisson   : Poisson model
 Gaussian  : Gaussian model
 LINear    : Linear model
 Cosine    : Cosine model
 Twolevel  : Two-level model
 Help      : Display menu
 Return    : Return to last menu
ROD.SET.CALC.ROUGH>
************************* SET SURFACE MODEL PARAMETERS ************************
 Element   : Element type of atom
 Xstart    : Start x-position
 XConstant : Multiplication factor of x-displacement
 XDisplace : Serial number of x-displacement parameterx2constant
 X2Constant: Multiplication factor of 2nd x-displ.
 X2Displace: Serial number of 2nd x-displacement par.
 Ystart    : Start y-position
 YConstant : Multiplication factor of y-displacement
 YDisplace : Serial number of y-displacement parametery2constant
 Y2Constant: Multiplication factor of 2nd y-displ.
 Y2Displace: Serial number of 2nd y-displacement par.
 Zstart    : Start z-position
 ZDisplace : Serial number of z-displacement parameterb1
 B1        : Serial # of in-plane Debye-Waller par
 B2        : Serial # of out-of-plane Debye-Waller paroccupancy
 Occupancy : Serial number of occupancy parameter
 Add       : Add an atom to model
 Delete    : Delete an atom from model
 Fullmodel : Show extended model yes/no
 List      : List atoms
 Help      : Display menu
 Return    : Return to main menu
ROD.SET.FIT>
******************************** SET PARAMETERS *******************************
 SCale     : Scale factor of theory
 SCALE2    : 2nd scale factor of theory
 Beta      : Roughness parameter beta
 SUrffrac  : Reconstructed-surface fraction
 Displace  : Value of displacement parameter
 B1        : Value of paral. Debye-Waller parameter
 B2        : Value of perp. Debye-Waller parameter
 Occupancy : Value of occupancy parameter
 List      : List parameters
 Help      : Display menu
 Return    : Return to main menu
ROD.SET.PAR>
**************************** SET DOMAIN PARAMETERS ****************************
 Ndomains  : Number of rotational surface domains
 Matrix    : Matrix elements of domain n
 Fractional: Calculate fractional coordinates yes/no
```

```
 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
 XMAxcont  : Upper bound on x value in patterson
 NXcontour : Number of steps along x in patterson
 YMIncont  : Lower bound on y value in patterson
 YMAxcont  : Upper bound on y value 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
 LALL      : Make all parameters free
 CALL      : 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
 NList     : 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
```

```
 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
ROD.FIT.CONTROL>
***************************** 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>
```