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REX - A PROGRAM FOR THE ANALYSIS OF X-RAY REFLECTIVITY DATA: USER GUIDE AND PROGRAMMER MANUAL

by

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REX - A Program for the Analysis of X-ray Reflectivity data:

User Guide and Programmer Manual

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ABSTRACT:

A FORTRAN program REX, which has been developed to facilitate the interpretation of X-ray reflectivity data, is described. The program allows the simulation of reflectivity profiles as a function of either incident angle or of energy. Factors such as anomalous dispersion, and surface and interface roughness are taken into account in the model. In addition, experimental data of reflectivity as a function of incident angle can be matched to user-supplied theoretical parameters by a least-squares refinement procedure. Experimental reflectivity data recorded at several X-ray wavelengths can be analysed simultaneously, thus eliminating certain experimental errors.

1. Introduction

This document acts as both a user and programmer guide for the ReX (reflectivity of X-rays) program. ReX [1] is an interactive menu driven program written in standard FORTRAN 77 on a SUN 4.0 workstation. The reflectivity model used is that of Parratt [2] who developed a recursion formula, starting from the Fresnel equations, describing the reflectivity from single or multilayer systems, see Sec. 3.1. ReX allows simulations as a function of energy or incident angle. In addition, a least-squares-fit can be performed by varying physical parameters proposed by the user (e.g. sample thickness and roughness) to match the theoretical curve to experimental data. Two roughness models are provided [3] [4] [5], these are described in detail in Sec. 3.3. Anomalous dispersion and absorption effects are incorporated using a database developed by Chromer and Liebermann [6] [7] [8].

Section 4. describes each of the options on the primary options menu in detail. Input file formats are also covered in this section.

Section 5. deals with the program structure and provides all the information necessary to enable efficient code modification.

2. Machine Specific Features

The program is written in standard FORTRAN 77 (American National Standard ANSI X3.9 1978). The only non-standard feature is the use of the "INCLUDE" command. The program has been compiled and linked using the SUN f77 compiler, release 1.3.

The system, unfortunately supported no linkable graphics objects. Hence, SAS graphics were used for the interactive plotting of data on the screen. Because SAS runs as a separate process, the only method of transferring data from ReX is to write it to an intermediate file. However, the interactive graphics calls have been restricted to two subroutines, PLOT1 and PLOT2, and these can be substituted by routines calling available packages.

A routine CLRSCR is used to clear the screen between menus; this is optional and can be left as a dummy routine if no screen clearing facility is provided.

Calculation using the recursion formula, REFMDL, introduces floating point underflow errors on many systems. Hence checks are introduced using a subroutine CHKCMP. Many computers automatically set values less than $1x10^{-72}$ to zero and the checks can be removed.

The least-squared fitting subroutine is from the NAG FORTRAN libarary: E04JAE.

3. Calculations

3.1. Reflectivity Calculations

The reflectivity model adopted uses the recursion formula derived by Parratt [2]. For n homogeneous layers, see Fig. 1, with plane-parallel interfaces the reflectivity coefficient is given by

$$R_{n-1,n} = a_{n-1}^{2}\left(\frac{R_{n,n+1} + F_{n-1,n}}{R_{n,n+1}F_{n-1,n} + 1}\right) \tag{1}$$

where

$$F_{n-1,n} = \frac{f_{n-1} - f_n}{f_{n-1} + f_n} \tag{2}$$

and

$$f_n = \left(\phi^2 - 2\delta_n - 2i\beta\right)^{1/2} \tag{3}$$

d_n is the layer thickness. δ and β are the real and imaginary decrements from unity of the complex refractive index, n, for X-rays in material, i.e. $n = 1 - \delta - i\beta$. ϕ is the incident angle and a_n is the amplitude reduction factor at half the perpendicular depth, d_n.

$$a_n = \exp\left(-i\frac{\pi}{2}f_n d_n\right) \tag{4}$$

For a medium comprising n-atomic species δ and β are calculated from

$$\delta = \frac{\lambda^2 r_e}{2\pi}\sum_{i=1}^{n} N_i(Z + f') \tag{5}$$

$$\beta = \frac{\lambda^2 r_e}{2\pi}\sum_{i=1}^{n} N_i f'' \tag{6}$$

where r_e is the classical electron radius, λ is the X-ray wavelength, Z_i is the atomic number and N_i is the atomic number density. Theroretical values of f' and f'', the

corrections to the atomic scattering factor, are those calculated and tabulated by D.T.Cromer[6] [7] [8]

Figure 3 (a) shows a reflectivity simulation for 500Å of Cr_2O_3 on Cr using the above model; the plateau region, critical angle and fringe region are labelled.

3.2. Atomic Number Densities

Facilities are provided to calculate the number densities of atomic species within a medium from either crystallographic parameters or mass number densities. The volume, V_m, occupied by one molecule can be calculated using the mass density, ρ, from the equation

$$V_m = \frac{M}{\rho N} \tag{7}$$

M is the molecular weight and N is Avogadro's number. For i atomic species, with n_i atoms in one molecule the atomic number density is,

$$N_i = \frac{n_i}{V_m} \tag{8}$$

For a unit cell with crystallographic parameters a, b, c, α, β and γ, the unit cell volume V_u is given by,

$$V_u = 2abc\left[\sin(S)\sin(S-\alpha)\sin(S-\beta)\sin(S-\gamma)\right]^{1/2} \tag{9}$$

where

$$S = \frac{\alpha + \beta + \gamma}{2} \tag{10}$$

Here, N_i is calculated from,

$$N_i = \frac{n_i z_u}{V_u} \tag{11}$$

where z_u denotes the number of formula units in the unit cell

3.3. Surface and Interface Roughness

Currently, two roughness models are provided. The first is an implementation of the classical scaler theory from Spizzichino [9] according to Cowley and Ryan [3]. In this model the Fresnel coefficients given in equation (2), are multiplied by a Debye-Waller-type factor containing the r.m.s. roughness of the surface, σ. F^*, the modified Fresnel coefficient, is given by

$$F^*_{n\,1,n} = F_{n\,1,n} \exp\left[-\frac{1}{2}\left(\frac{4\pi\sigma}{\lambda}\sin\phi\right)^2\right] \tag{12}$$

In the second approach, developed by Névot and Croce[4] [5], roughness is modelled as a local variation in the refractive due to the modifcation of composition, or density. Hence at the surface the refractive index varies as a function of depth according to:

$$n(z) = 1 + (n_1 - 1)F_{erf}(z) \tag{13}$$

where F_{erf} is the error function

$$F_{erf}(z) = \frac{1}{\sigma_1\sqrt{2\pi}}\int_{-\infty}^{z}\exp\left(\frac{-z^2}{2\sigma_1^2}\right)dz \tag{14}$$

The parameters used in the REX model are δ and β which are modified at each interface such that:

$$\delta(z) = \delta_1 + (\delta_2 - \delta_1)F_{erf}(z) \tag{15}$$

$$\beta(z) = \beta_1 + (\beta_2 - \beta_1)F_{erf}(z) \tag{16}$$

3.4. Instrumental Resolution

The effect of beam divergence is to dampen the Kiessig fringe oscillations. During the fitting of reflectivity data the fringe contrast is reduced by increasing the values for surface and interface roughness. To avoid artificially high roughness values, instrumental resolution effects must be included in the model ReX incorporates these effects by assuming that beam has a divergence and a specific beam profile, e.g. Gaussian or square. For each incident angle, the reflectivity is the calculated for each point on the beam profile and the average calculated. This is represented mathematically as:

$$R_0 = \frac{1}{n}\sum_{n/2}^{-n/2} R(\theta + n\Delta\theta) \tag{17}$$

The section uses simulations to illustrate important points Figure 2 shows a schematic diagram of a Cr_2O_3 surface oxide on a Cr layer deposited onto glass, with the layers numbered as they would be specified by the user on input.

4.1. Sample Attribute Types

There are three types of attributes associated with a user defined sample structure: general, layer and atom.

General attributes refer to those parameters external to the physical system, i e X-ray wavelength, direct beam intensity, background constant, zero point error and instrumental resolution.

Layer attributes are associated with in individual sample layers, i.e. thickness, and roughness.

Atom attributes are specified for all atom types within each sample layer. These include the atomic number density, and the real and imaginary parts of the anomalous scattering factors.

4.2. Data Representation

When plotting theoretical curves or experimental data within ReX the user my want to emphasize a particular feature, e.g. the plateau region or the Kiessig fringe system. Logging the data enhances the fringes would bias a fit towards this region thus, in effect, provides a method weighting the data. Three further representations are included, demonstrated in Figure 3, in addition to the standard (R Represents the reflectivity) :

- **$LOG_{10}(R)$** Figure 3(b) shows a plot with the reflectivity as a LOG_{10}.
- **$R^*(2\phi)^n$** A second method of weighting the fringes is shown in figure 3(c) Where 2ϕ is the angle of the X-rays to the direct beam after reflection and n is an integer value, usually selected as 4.
- **$LOG_{10}(R^*(2\phi)^n)$** as for the 2nd method two but logged, see figure 3(d)

4.3. Primary Options Menu

The primary options menu is the top level menu presenting 10 options to the user In this section each option with its associated sub-options is covered in some detail A

universal option 100, i.e one that can be entered from any menu, returns control to the previous menu, or ends the program if the menu is at the top level. A second universal option 99 is covered at the end of the section, which invokes a special program editor.

4.3.1. OPTION 1 - Program I/O

The following sub-options are presented.

1) READ VALUES FROM FILE

Prompts the user for an input file name containing a proposed sample structure to be fitted to experimental data, to generate reflectivity simulations An example of the format is given in Appendix A. it is important to provide information in the order shown in the example If the program is using the CROSSEC database the values for f' and f" are ignored '!' represents a comment line and '/' indicates the start of a new layer.

2) ENTER VALUES AT TERMINAL

The user is prompted for the sample details at the terminal

3) READ EXPERIMENTAL DATA SET

Prompts for an experimental data file name. The user supplies the columns to read, with a constant multiplier and the start line number. If multiple data sets are to be fitted they must be read together.

4)SAVE CURRENT VALUES TO A FILE

Saves sample details to a file which can be read in at a later stage.

4.3.2. OPTION 2 - Manipulate the Experimental Data Set

If fitting multiple data sets the user is prompted for the data set number for all these options 1- - 3

1) CONVENTIONAL PLOT Y VERSUS X

Plots experimental data set on a conventional scale Y versus X

2) LOG10(Y) VERSUS X

Plots experimental data set as LOG10(Y) VERSUS X

3) Y*(CHI**N) VERSUS X

Plots experimental data set as Y*(CHI**N) VERSUS X.

4) LOG10(Y*(CHI**N)) VERSUS X

Plots experimental data set as LOG10(Y*(CHI**N)) VERSUS X.

5) EXAMININE THE DATA POINTS AT THE TERMINAL

Displays experimental data points on the screen.

6) SELECT THE DATA RANGE

Prompts for a data range for display of experimental points and for fitting.

7)CLEAR THE DATA RANGE

Clears a data range.

4.3.3. OPTION 3 - Change Mode

1) FIT ATOMIC NUMBER DENSITY

Program mode selected to fit atomic number densities using values of f' and f" from CROSSEC (default mode)

2) FIT DELTA AND BETA

Program mode selected to fit the delta and beta values.

3) NORMAL MODE

Program not in multilayer mode.

4) MULTILAYER MODE

Program generates extra layers by copying existing ones depending on the users requirements.

5) COWLEY AND RYAN

Uses Debye-Waller type roughness factor.

6) ERROR FUNCTION - NEVOT AND CROCE

Uses the error function for roughness.

4.3.4. OPTION 4 - Det. Atomic No. Densities

1) SAMPLE LAYER - CELL PARAMETERS KNOWN

Determines atomic concentrations for a specified sample layer from crystallographic cell parameters.

2) SAMPLE LAYER - MASS DENSITY KNOWN/KGM-3

Determines atomic concentrations for a specified sample layer from a mass density value.

3) ANOTHER SYSTEM - CELL PARAMETERS KNOWN

Determines atomic concentrations for a specified system from crystallographic cell parameters.

4) ANOTHER SYSTEM - MASS DENSITY KNOWN/KGM-3

Determines atomic concentrations for a specified system from a mass density value.

4.3.5. OPTION 5 - Det. Delta/Beta/Critical values

1) CRITICAL ANGLE/DELTA/BETA

Determines delta, beta and the critical angle for a specified sample layer and energy.

2) CRITICAL ENERGY

Determines the critical aenergy for a specified sample layer and angle.

4.3.6. OPTION 6 - Simulations

For each of these simulations the current sample details are used. If several wavelengths have been specified in the input file the user is prompted for the number to use.

1) CONVENTIONAL (R) VERSUS ANGLE/DEGREES

Reflectivity simulation for a specified angular range displayed in a conventional plot.

2) LOG_{10}(R) VERSUS ANGLE/DEGREES

Reflectivity simulation for a specified angular range displayed as $LOG_{10}(R)$.

3) R*(CHI**N) VERSUS ANGLE/DEGREES

Reflectivity simulation for a specified angular range displayed as $R*(CHI)^N$, where CHI = 2ϕ and N is an integer.

4) LOG_{10}(R*(CHI**N)) VERSUS ANGLE/DEGREES

Reflectivity simulation for a specified angular range displayed as $LOG_{10}(R*(CHI)^N)$, where CHI = 2ϕ and N is an integer.

5) CONVENTIONAL (R) VERSUS ENERGY

Reflectivity simulation for a specified energy/wavelength range.

6) TRANSMITTED WAVE INTENSITY AT SURFACE

Transmitted X-ray intensity at the sample surface as a function of angle.

7) PENETRATION DEPTH

Calculates the penetration depth within a selected layer as a function of incident angle.

8) BETA VERSUS ENERGY

Beta as a function of energy/wavelength for a specified sample layer.

9) DELTA VERSUS ENERGY

Delta as a function of energy/wavelength for a specified sample layer.

10) DELTA AND BETA VERSUS SAMPLE DEPTH (ERROR FUNCTION ONLY)

Plots the refractive index profile as a function of depth perpendicular to the sample surface.

4.3.7. OPTION 7 - Conditional fit

When fitting multiple data sets the user is able to specify which should be included in any fit. Following a fit the quality is shown and an indication of whether a true minimum has been reach. The user then has the option to accept or reject the new sample parameters

1) CONVENTIONAL REFLECTIVITY (R)

Perform an unconditional fit as a function of angle in a convention representation.

2) LOG_{10}(R)

Perform an unconditional fit as a function of angle in $LOG_{10}(R)$.

3) R * (CHI**N)

Perform an unconditional fit as a function of angle in $R*(CHI**N)$, where $CHI = 2\phi$ and N is an integer.

4) LOG_{10}(R *(CHI**N)) - COWLEY AND RYAN

Perform an unconditional fit as a function of angle in $LOG_{10}(R*(CHI**N))$, where $CHI = 2\phi$ and N is an integer.

4.3.8. OPTION 8 - Compare EXP./THEO. Curves

As for OPTION 8 but no fit is performed, the experimental points and the theoretical curve are displayed together at the terminal. This helps the user to establish a good starting model.

4.3.9. OPTION 99 -Display/Edit Sample/Fitting Details

Invokes a special ReX editor for modifying sample parameter values and selecting and deselecting fit parameters. Each parameter type has an identifying number as listed below:

1 - X-ray wavelength
2 - Direct beam intensity
3 - Background constant
4 - Zero point error
5 - Instrumental resolution
6 - Layer thickness
7 - Layer roughness
8 - Atomic number density
9 - Real part of the Anomalous scattering factor
10 - Imaginary part of the Anomalous scattering factor

The commands are
DS - Display sample details

MV - Modify a sample parameter
IP - Include a file parameter
RP - Remove a fit parameter
DP - Display the list of fit parameters and bounds
MB - Modify the bounds of a fit parameter
CP - Clear the whole fit parameter list
HP - Help information
EX - Exit from editor to menus

Two examples are provided, for clarity the users responses are in bold.

Example 1

Modify the value for the wavelength

ENTER COMMAND >

MV 1

CURRENT VALUE = 1.542

ENTER NEW VALUE >

1.488

Example 2

Include the atomic concentration of the first atom in layer 2 as a fit parameter:

ENTER COMMAND >

IP 8

ENTER LAYER NUMBER AND ATOM NUMBER >

2 1

PARAMETER VALUE = 0.0913

ENTER LOWER AND UPPER BOUNDS >

0.08 0.095

NEW FITTING PARAMETER INCLUDED

5. Programmer's Manual

This section contains information of interest to the programmer. Data structures, the configuration file and the subroutine hierarchy are covered. Program structure diagrams are located in Appendix C, and are refered to when necessary. Extensive used has been made of the FORTRAN PARAMETER statement in include files. This means that modification of a parameter value, for example the maximum number of sample layers (currently set to 100), need only be made in the appropriate include file. Throughout the code variable names follow a standard corresponding to the type:

REAL*8	R——
INTEGER*4	I----
CHARACTER*?	C——
COMPLEX*16	X——

5.1. Data Structures

Rex Comprises 7 FORTRAN include files all with the suffix ".H":

CONST.H	mathematical constants and atomic masses
MODE.H	current program mode settings
PARAM.H	parameter statements for SMPDEF and DATDEF
SMPDEF.H	user specified sample details
DATDEF.H	experimental file variables
PARPAR.H	parameter statements for CODPAR
CODPAR.H	fitting parameter table with attributes

5.1.1. CONST.H

Contains mathematical constants and array with elemental symbols and atomic masses (array member numbers correspond to the atomic numbers). Common statements are named as follows:

CONSTS	mathematical constants
MELEM	atomic masses
CSELEM	elemental symbols

5.1.2. PARAM.H

PARAM contains PARAMETER statements for values used by SMPDEF and DATDEF. These are currently set to:


```
IMXDTA =10000   !Maximum number of data points
ICUDS  =1       !Number referring to the first file
IMXDS  =3       !Maximum number of experimental data sets
INTOR  =2       !Interpolation order - input parameter to CROSSEC database
IMXLY  =100     !Maximum number of sample layers
IMXAT  =6       !Maximum number of atom types per layer
IMXPT  = 10000  !Maximum number of points in a plot
```

The simulation types are with following definitions:

```
THSCAN =1       !Simulation as a function of angle
WVSCAN=2        !Simulation as a function of wavelength/Å
ENSCAN =3       !Simulation as a function of energy/KeV
```

The Data representations described in Sec. 4.2 correspond to the following PARAMETER values:

```
CHSCAN =4       !R*(2φ)^n
LGSCAN =5       !LOG10(R)
LCSCAN =6       !LOG10(R*(2φ)^n)
```

The following unit numbers are reserved by ReX:

```
ICROSS  =1      !CROSSEC data file
IFILE   =2      !INPUT/OUTPUT sample/experimental data
IRD     =5      !Input from screen
IWRT    =6      !Output to screen
ITMP    =9      !Intermediate data file for SAS graphics
```

5.1.3. SMPDEF.H

Sample details defined by the user for simulations are for refinement during a least-squares-fit. Note that some of the variables are defined per file using the PARAMETER IMXDS The arrays are as follows:

General physical parameters

```
RLAMBDA(IMXDS)      !Wavelength/Å
RIO(IMXDS)          !Incident X-ray intensity
RBG(IMXDS)          !Background constant
RZROFF              !Zero point error
RINRES              !Instrumental resolution
```

Layer Parameters:

ISMLYR	!Number of layers
RROUGH(IMXLYR)	!Roughness/Å
RTHICK(IMXLYR)	!Layer Thickness/Å
RDELTA(IMXLYR)	!Delta
RBETA (IMXLYR)	!Beta

Atom parameters:

IATNOS(IMXLYR)	!Number of atom types per layer
RATP (IMXLY,IMXAT)	!Atomic concentration
IFP (IMXLY,IMXAT)	!Real part of the anomalous scattering factor
IFPP (IMXLY,IMXAT)	!Imaginary part of the anomalous scattering factor
IATQUN(IMXLY,IMXAT)	!Number of atoms i e stoichiometry
IATZ (IMXLY,IMXAT)	!Atomic numbers
CATS (IMXLY,IMXAT)	!Atomic symbols

Values used in multilayer sample definitions

IMLTRP(IMXLYR)	!Number of times to repeat
IMLTPR(IMXLYR)	!Number of prior layers to include

5.1.4. DATDEF.H

Contains variables used for experiment data sets. Common name is DATA.

ITOTAC	!Total number of experimental data sets read
IACTDS(IMXDS)	!Index of data sets activated for fitting

Data as read from an input file

RXDATA(IMXDTA,IMXDS)	!X-axis values
RYDATA(IMXDTA,IMXDS)	!Y-axis values
INODTA(IMXDS)	!Number of points read

Data range selected for fitting, can be different for each data set

ILDTA(IMXDS)	!Lower limit
IUDTA(IMXDS)	!Upper limit

Data after range has been selected - these arrays are passed to the fitting routines

RXEXP(IMXDTA,IMXDS)	!X-axis values
RYEXP(IMXDTA,IMXDS)	!Y-axis values
IEXDTA(IMXDS)	!Number of points read

5.1.5. PARPAR.H

PARPAR contains PARAMETER statements used by variables defined in CODPAR and parameters used in the module EDTR.

Number of different attribute types, see Sec. 4.1 for a list.

INOVGN =5	!General attribute
NOVLY =4	!Layer attributes
INOVAT =3	!Atom attributes
INOVDS =3	!Number of general attributes which have different values depending in the file number i.e. wavelength, intensity of direct beam, background constant

ILYEND =INOVGN+INOVLY	!End of layer attributes used for display purposes
IATEND =INOVGN+INOVLY+INOVAT	!End of atom attributes used for display purposes
INOPAR =20	!Max number of selected fitting parameters
ISTAR =2000	!Length of character array used when displaying sample details. Contains a blank or asterisk depending on which parameter is selected for fitting.

Attribute type parameters:

GEN ='GE'	!General
CLAYER ='LA'	!Layer
CATOM ='AT'	!Atom

Commands used by EDTR:

CDSPS ='DS'	!Display sample details
CDSPP ='DP'	!Display list of fit parameters
CMODV ='MV'	!Modify sample value
CINCP ='IP'	!Include a fit parameter
CREMP ='RP'	!Remove a fit parameter
CCLRP ='CP'	!Clear the list of fit parameters
CMODB ='MB'	!Modify the bounds of a fit parameter
CHELP ='HP'	!Invoke help menu
CEXIT ='EX'	!EXIT from EDTR

5.1.6. CODPAR.H

This include file contains the variables used for performing a least-squares fit. The details of the sample parameters to be fitted are held in a table. The current values of these parameters are passed into the NAG library fitting routines. COMMON names used are CODES, FTYPE,NAMES and BOUNDS.

CSTPAR(ISTAR)	!Character array - for display purposes only
CGNAME(INOVGN)	!General attributes, initialised in INIT - for display purposes only
CLNAME(INOVGN)	!Layer attributes, initialised in INIT- for display purposes only
CANAME(INOVAT)	!Atom attributes,initialised in INIT - for display purposes only

The following arrays represent the table of selected fit parameters. The array number INOPAR represents the index to the parameter in the list.

IPATOT	!Number of parameters in the table
CATPAR(INOPAR)	!Two character string representing attribute type - see PARPAR (GE/LA/AT)
ICDPAR(INOPAR,4)	!For each array entry there are 4 values saved to indicate which physical sample parameter is to be fitted: 1) Attribute number 1 -> 10 see Sec. 4.3.9. 2) Layer number 3) Atom number 4) Data set number
LSPBD(INOPAR)	!Bound logical
RBOUND(INOPAR,2)	!Values for the bounds 1) Lower 2)Upper
RXFIT(INOPAR)	!Array containing the actual values of each of the fit parameters passed to NAG library
RSCALE(INOPAR)	!Scaling factors associated with RXFIT
IFTTYP	!Type of data representation
IPOWER	!Power used

5.1.7. MODE.H

Contains current ReX status and uses the COMMON name PLOTS:

Parameter values:

IFPFPP =1	!Model uses f' and f" as a starting point
IDELTA =2	!Model uses δ and β as a starting point
IMULTI =3	!Multilayer mode
IGAUSS =1	!Use Debeye-Waller type roughness factor
INEVCR =2	!Uses Nevot and Croce error function

Plotting options:

CKSAS(4)	!SAS filenames for plotting one file
CKCF(4)	!SAS filenames for plotting two data sets
CCSAS(4)	!Terminal Type names
ITERM	!Current terminal type

Status values:

ITOTDS	!Total number of data sets read
ITOTSM	!Number of different wavelengths active
IMODE	! Model selected (IFPFPP/IDELTA/IMULTI)
IROUGH	!Roughness model selected

5.2. Configuration file

This is an ASCII data file read in by INIT containing a list of elements with their atomic masses, in order of ascending atomic number. See Appendix B for the format.

5.3. Modules and Subroutines

The source code for these is in the partitioned file called REX2.FORT. Each member file contains a module, which is in 10 files with the suffix ".f" :

IOSMDT	Input/output of sample parameters and experimental data (Option 1)
EXDATA	Manipulation and plotting of experimental data (Option 2)
REX	MAIN routine /initialisation/miscellaneous/plotting/ reflectivity model (Option 3)
ATNODN	Calculation of atomic concentrations (Option 4)
CRTVAL	Determination of critical angles (Option 5)
CRVGEN	Simulations (Option 6)
FIT	Conditional fitting (Options 7 and 8)
FPFPP	CROSSEC database
ERROR	Nevot and Croce error function
EDTR	ReX editing facilities (Option 99)

This next sections give a brief outline of the function of each subroutine in the various modules.

5.3.1. REX.F

***Main routine* - see figure C.1.**

MAIN

Displays the primary options menu and transfers program execution to the selected module.

***Initialisation* - see structure figure C.2.**

INIT

Initialises mathematical constants and terminal types. Sets up the character array CGNAME used for display purposes and defined in the include file CODPAR.

CNFINT

Reads atomic symbols and masses from the data file CONFIG.DATA - the full path name to the file is used in this routine.

PARINT

Initialises the character array CSTPAR (include file CODPAR) used to place an asterisk beside selected fitting parameters.

Miscellaneous Routines

MASK

Outputs menus to the screen and prompts for selection of valid options.

CHARLU

Converts character strings to uppercase.

CLRSCR

Clears the screen - currently a dummy routine.

CONT

Waits for terminal input.

FDNOMS

Verifies an atomic symbol is valid and returns the atomic mass. If invalid a non-zero return code is set.

CHMODE

Changes program modes relating to roughness models and single/multilayer modes.

TITLE

Writes a title page on the screen.

SELDS

When fitting multiple data sets prompts for and verifies a file number.

Plotting Routines

RDPLOT

Prompts user to specify start, end and resolution for a plot. If the maximum number of plotting points is exceeded the resolution is automatically recalculated.

PLOT1

Simple X v Y plot

PLOT2

As for PLOT1 but displays two data sets.

Reflectivity Model

DETDB

Calculates delta and beta from the anomalous scattering factors.

REFLCT

Parratt's reflectivity model.

GUARGH

Cowley and Ryan, Debye-Waller type roughness factor.

CHKCMP

Called by REFLCT to avoid underflow errors while manipulating complex variables (machine specific).

5.3.2. IOSMDT.F

IODATA

Displays the menu on the screen and transfers execution to the selected subroutine.

COPY

Allows layers to be repeated when reading from a file - facilitates in setting up multilayers. If the program is set to multilayer mode then the copy is made before each fit or simulation. If ReX is in normal mode the copy is executed on reading the input file.

RDPARM

Allows input of sample details at the terminal.

CHKVAL

If blank entered sets a specified default value.

WRPARM

Saves current sample details to a file.

FLPARM

Reads the sample details from an input file.

FDSTRG

Used by FLPARM to find a non-comment line in the input file.

RDDATA

Reads in experimental file from an input file.

5.3.3. EXDATA.F

See figure C.4.

EXDTA

Places menu onto screen and transfers execution to the selected subroutine (EXMAN/DSPDTA/SELRGN)

EXDMAN

Plot the experimental data according to the selected data representation.

DSPDTA

List the data points on the screen

SELRGN

Select a data region to be fitted/remove a selected region.

FDDTNO

For a specified angle find the array index number.

5.3.4. ATNODN.F

See figure C.5

ATNODN

Places a menu on the screen and transfers execution to the selected routine (CRTAN1/CRTAN2).

CRTAN1

Using the crystallographic cell parameters the unit cell volume, the electron density, the critical angle and the atomic concentrations are determined.

CRTAN2

Using the mass density (kgm^{-3}) the unit cell volume, the electron density, the critical angle and the atomic concentrations are determined.

5.3.5. CRTVAL.F

See figure C.6.

CRITG

Places a menu on the screen and transfers execution to the selected subroutine

CRITA

For a specified X-ray energy and sample layer, determines delta, beta and the critical angle for total external reflection

CRITE

For a specified incident angle and sample layer, determines delta, beta and the critical energy for total external reflection

5.3.6. CRVGEN.F

See figures C.7., C.10 and C.12

REFMDL

For an array of incident angles the reflectivity is determined

CRVSEL

Places a menu on the screen and transfers execution to the selected subroutine (INTAN/INTEN/TRNPRF/PENPRF/INTPRF)

INTEN

Intermediate routine to simulations as a function of energy, presents masks and transfers execution

INTAN

Intermediate routine to RFPRFA from CRVSEL, .i.e. reflectivity simulations as a function of angle, presents masks and transfers execution.

INTRFA

Intermediate routine to RFPRFA from CFDATA and DIAG as a function of angle.

INSRES

Includes the effects of instrumental resolution - treating the profile as a square function.

RFPRFA

Generates reflectivity profile for a specified angular range.

RFPRFE

Generates reflectivity profile for a specified energy range.

INTCR

Intermediate routine to Chromer and Liebermann database CROSSEC calls FPFPP.

PENPRF

Determines penetration depth.

TRNPRF

Calculates the transmitted wave intensity in the top layer of the sample as a function of incident angle.

SVSIM

Save a simulation to a two-column data file.

CHWGHT

An array of points (angle v reflectivity) is modified to the selected data representation, indicated by the input flag ISCTYP.

5.3.7. FIT.F

See figures C.8 and C.9.

FITSEL

Places a menu onto the screen to select the type of data representation used in the fit. Then calls BDFIT.

BDFIT

Performs a bounded fit using the NAG routine E04JAE.

FUNCT1

User supplied routine to calculate the sum of the squares between experimental and theoretical data points, called by the NAG routine E04JAE.

DIAG

Provides diagnostics on the previous fit.

CFSEL

Places a menu on the screen to select the data representation used in a direct comparison between theoretical and experimental data sets, then calls CFDATA.

CFDATA

Compares theoretically simulations with experimental data points. Provides a value for the sum of squares.

SCALE

Scales parameters to be fitted to values between -1 and 1. The scaling factors are held in common memory to reconvert the final values.

5.3.8. FPFPP.F

FPFPP

Extracts anomalous scattering factors from CROSSEC database.

5.3.9. ERROR.F

See figure C.11.

LAYER

Places menu on the screen giving the option of including or removing sample layers for the error function or multilayer mode.

PROFILE

Plots delta and beta as a function of the sample depth.

SAVLAY

Saves current sample layer details.

REMLAY

Returns sample layers to their original specifications.

ERROR

Generates the intermediate error function layer.

MULTI

Generates multilayers in multilayer mode.

SHIFT

Used by ERROR to shift sample layers.

5.3.10. EDTR.F

See figure C.12

SMPDET

Control program for manipulating the sample details, including the removal and specification of fit parameters.

HELP

Provides an on-line help for editor.

DSPSMP

Displays current sample details at the terminal, with the selected fitting parameters labelled with an asterisk.

DSPPAR

Display a list of fitting parameters with bounds.

VALCHG

Verifies that the sample parameter selected for modification or inclusion as a fit parameter is valid.

MODSTR

Updates the array CSTPAR containing blank characters or asterisks for labelling fitting parameters on display the sample details.

PARLST

Adds a fit parameter to the list by recording its attributes, GENERAL/LAYER/ATOM, and the file its associated with, if multiple file fitting.

MODB

Alows the bounds of fit parameters to be modified.

DECVAL

Inserts a value into the sample details held in common memory for a specified sample parameter (i.e. requires attribute type, layer number, atom number). Also extracts the current value in the same way.

STATUS

Places the current program status onto the screen, i.e fit mode, roughness model, number of data sets etc.

6. References

[1] T.A.Crabb, K.J.Roberts and P.N.Gibson, Daresbury Preprint DL/SCI/P845E (1992), Submitted to Computer Physics Communications

[2] L.G:Parratt, Phys. Rev. **95** (1954) 1593

[3] R.A.Cowley and T.W:Ryan, J. Phys. D. **20** (1987) 61

[4] P.Croce and L.Névot, Revue Phys. Appl. **11** (1976) 113

[5]L.Névot and P.Croce,Revue Phys Appl. **15** (1980) 761

[6] D.T.Cromer, Acta Cryst **18** (1965) 17

[7] D.T.Cromer and D.A.Lieberman, J Chem Phys **53** (1970) 1891

[8] D.T.Cromer, J.Appl. Cryst. **16** (1983) 437

[9] P.Beckmann and A.Spizzichino, in: The Scattering of Electromagnetic Waves from Rough Surfaces (Pergamon, New York, 1963)

Figure Headings

Figure 1. X-ray reflectivity and refraction for n-homogeneous layers. Note that the angles are greatly exaggerated to show the effects of refraction.

Figure 2. Example sample specification for Cr_2O_3 surface layer on a deposited Cr film on glass. (σ-roughness, d-thickness, n-refractive index and I_o-incident X-ray intensity).

Figure 3. Types of data reprensentation provided by ReX.

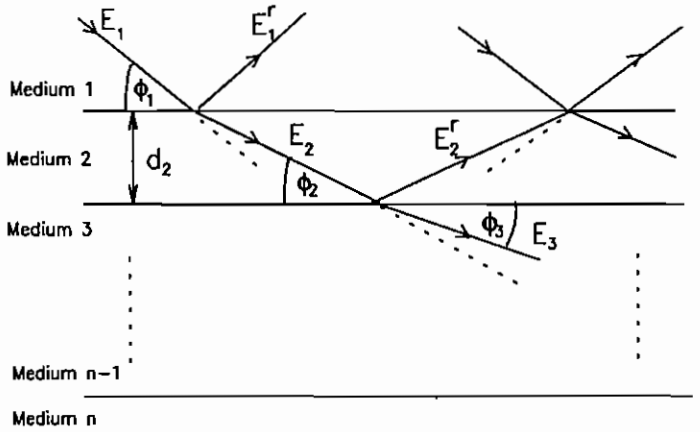

Fig. 1

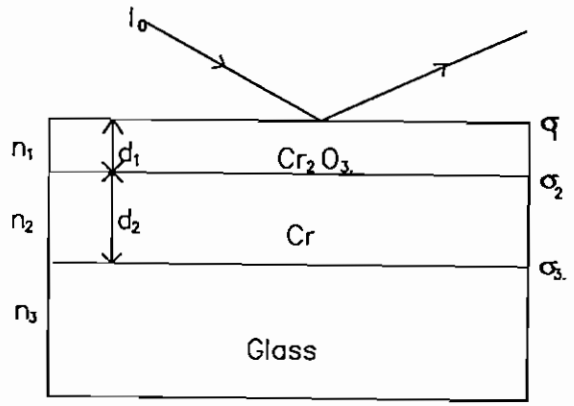

Fig. 2.

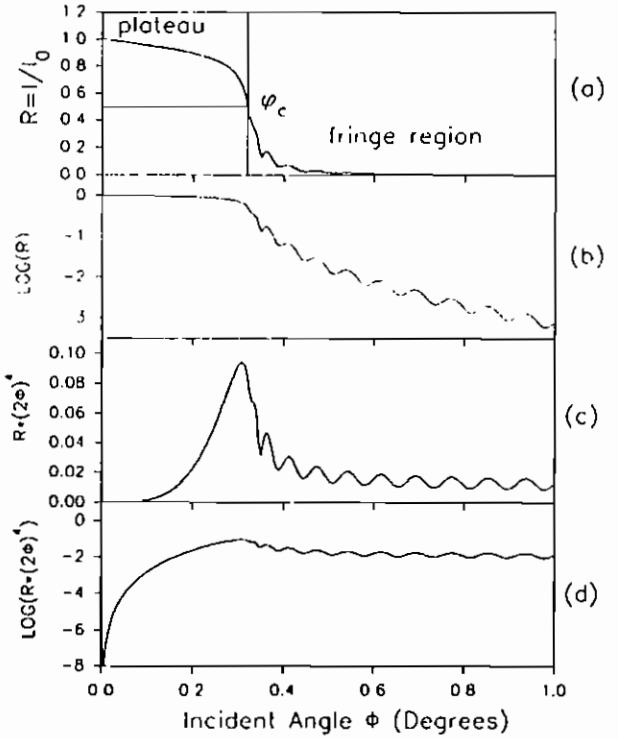

Fig. 3.

APPENDIX A

```
! Example input file for ReX
!
! NUMBER OF WAVELENGTHS - IF FITTING MULTIPLE PATTERNS
 2
!
! WAVELENGTHS / Å
     1.54200       1.39000
!
! DIRECT BEAM INTENSITYS / C.P.S
   1.00000     0.10000
!
! BACKGROUND CONSTANT/C.P.S
     0.000       0.0000
!
! ZERO POINT ERROR/DEG
  0.00000  0.00000
!
| INSTRUMENTAL RESOLUTION/DEGREES|
0.01
!
! LAYER NUMBER 1 - Cr layer
!
! LAYER THICKNESS/A | ROUGHNESS/A | REPEAT NUMBER | INCLUDE
PREVIOUS |
   1054.68750  14.53567        1  0
! DELTA | BETA | (Zero - If fitting Atomic Number densities)
   0.21058E-04
   0.21664E-05
!
! ATOMIC SYMBOL | NO. DENSITY/KGM-3 | ATOM RATIOS|
CR   0.08300  1
/
!                                                    |
! LAYER NUMBER 2 - Glass Substrate
!
! LAYER THICKNESS/A | ROUGHNESS/A | REPEAT NUMBER | INCLUDE
PREVIOUS |
 1000000.00000   0.03202        1  0
! DELTA | BETA | (Zero - If fitting Atomic Number densities)
   0.10809E-04
   0.14187E-06
!
! ATOMIC SYMBOL | NO. DENSITY/KGM-3 | ATOM RATIOS|
SI   0.03375  1
O    0.06625  2
/
```


APPENIDIX B

Configuration file format:

```
!-----------------------------------------------------------------
!   THIS FILE CONTAINS CONFIGURATION DETAILS FOR THE FITTING
!   PROGRAM REX
!   IMPORTANT - '!' IN THE FIRST COLUMN INDICATES THIS IS
!                    A COMMENT LINE AND WILL BE IGNORED BY THE PROGRAM
!   THE FILE IS READ SEQUENTIALLY THUS THE ORDER OF THE LINES
!   IS IMPORTANT.
!-----------------------------------------------------------------
!  ELEMENTS WTH THEIR ATOMIC MASSES
!*!****.*****!**!****.*****!**!****.*****!**!****.*****!**!****.*****!
H     1.00800 HE    4.00300 LI    6.94000 BE    9.01300 B    10.82000
C    12.01100 N    14.00800 O    16.00000 F    19.00000 NE   20.18300
NA   22.99100 MG   24.32000 AL   29.98000 SI   28.09000 P    30.97500
S    32.06600 CL   35.47500 AR   39.94400 K    39.10000 CA   40.08000
SC   44.96000 TI   47.90000 VA   50.95000 CR   52.01000 MN   54.94000
FE   55.85000 CO   58.94000 NI   58.71000 CU   63.54000 ZN   65.38000
GA   69.72000 GE   72.60000 AS   74.91000 SE   78.96000 BR   79.91600
KR   83.80000 RB   85.48000 SR   87.63000 Y    88.92000 ZR   91.22000
NB   92.91000 MO   95.95000 TB   99.00000 RU  101.10000 RH  102.91000
PD  106.40000 AG  107.88000 CD  112.41000 IN  114.82000 SN  118.70000
SB  121.76000 TE  127.61000 I   126.91000 XE  131.30000 CS  132.91000
BA  137.36000 LA  138.92000 CE  140.13000 PR  140.92000 ND  144.27000
PM  145.00000 SM  150.35000 EU  152.00000 GD  157.26000 TB  158.93000
DY  162.51000 HO  164.94000 ER  167.27000 TM  168.94000 YB  173.04000
LU  174.99000 HF  178.50000 TA  180.95000 W   183.86000 RE  186.22000
OS  190.20000 IR  192.20000 PT  195.09000 AU  197.00000 HG  200.61000
TL  204.39000 PB  207.21000 BI  209.00000 PO  210.00000 AT  210.00000
RN  222.00000 FR  223.00000 RA  226.05000 AC  227.00000 TH  230.05000
PA  231.00000 U   138.07000
```

APPENDIX C

ReX structure diagrams, excluding miscellaneous routines.

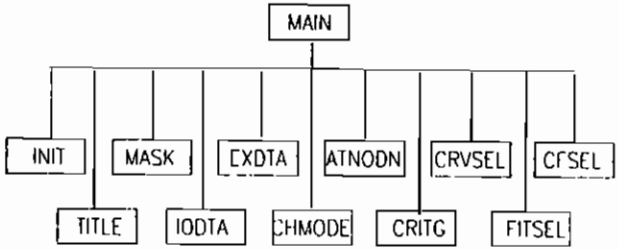

Figure C.1.

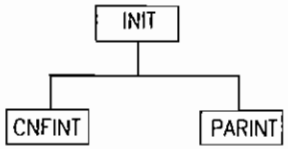

Figure C.2.

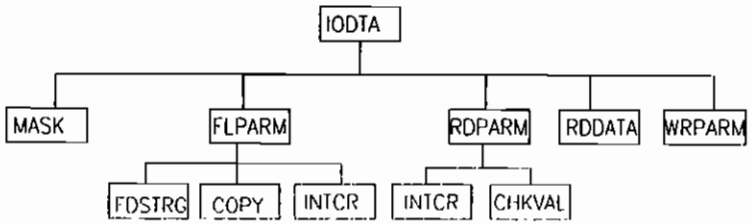

Figure C.3

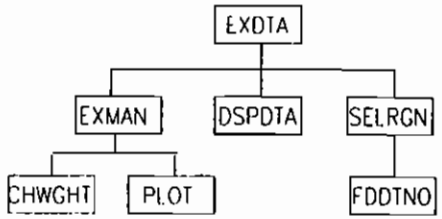

Figure C.4

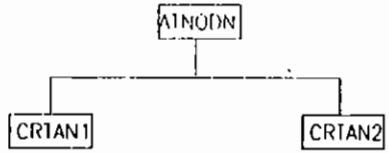

Figure C.5

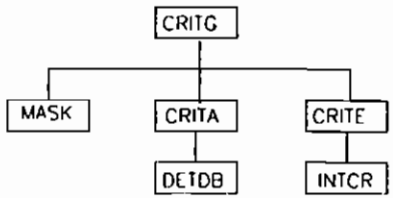

Figure C.6.

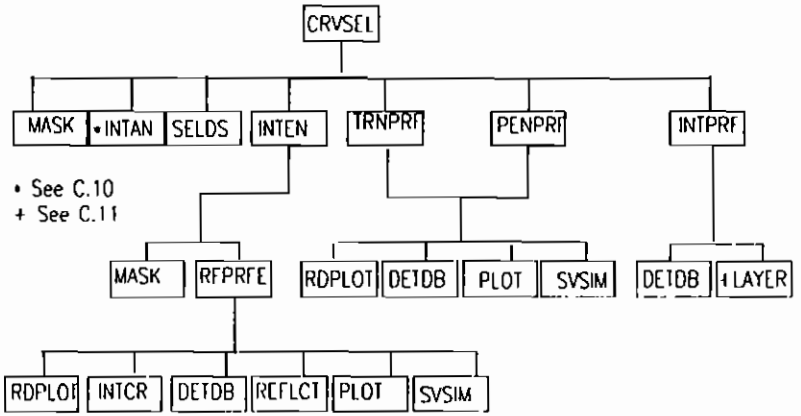

Figure C.7.

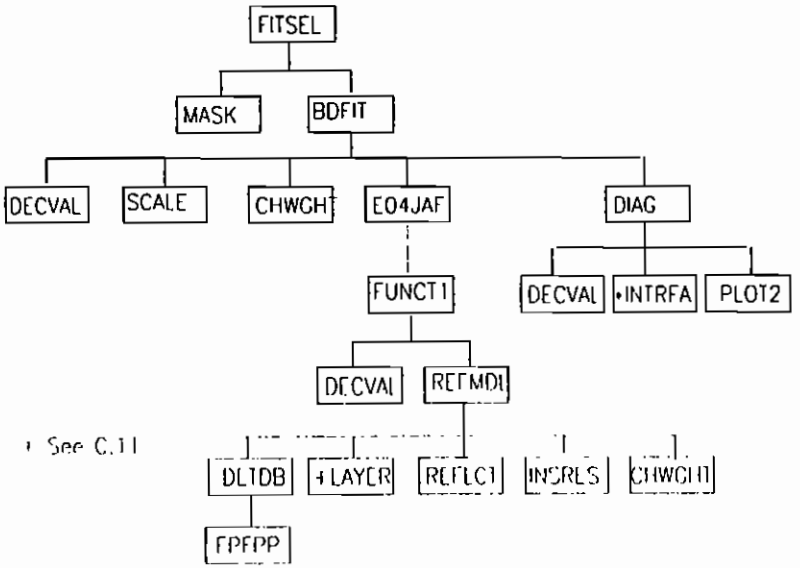

Figure C.8

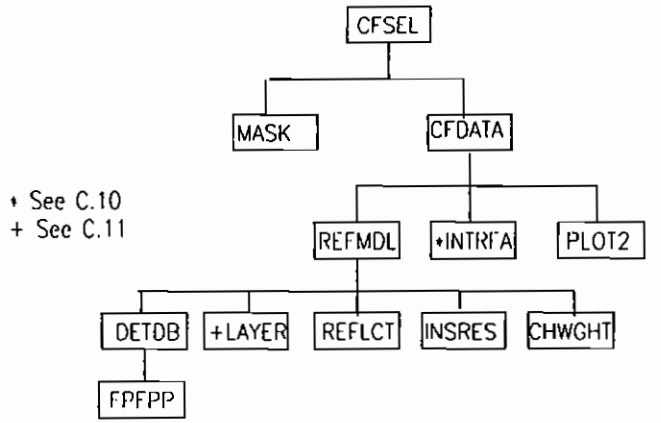

Figure C.9

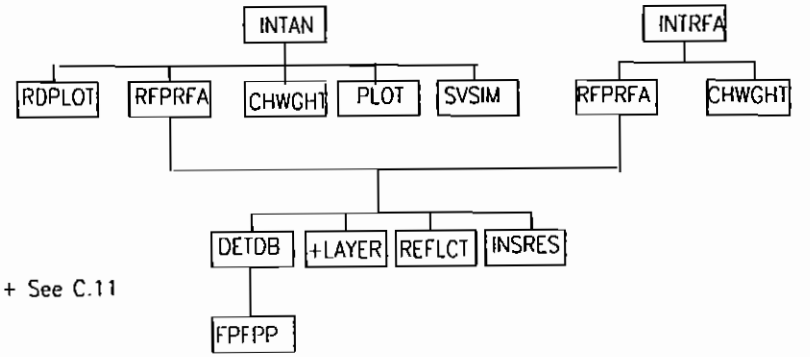

Figure C.10

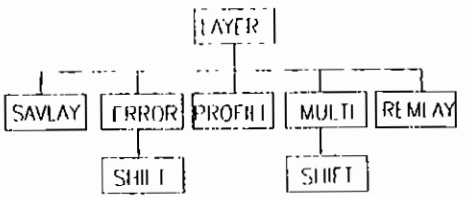

Figure C.11