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SOFTWARE FOR THE ANALYSIS OF ENERGY-DISPERSIVE POWDER
DIFFRACTION DATA

by

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Software for the analysis of energy-dispersive powder diffraction data.

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Abstract

This report describes the software available at Daresbury Laboratory for the analysis of energy-dispersive powder diffraction data. This report is intended as a guide for users of the energy-dispersive powder diffraction facility.

Contents

1 Introduction

The use of energy-dispersive powder diffraction (EDPD) at the Daresbury Synchrotron Radiation Source (SRS) has increased dramatically since the advent of a permanent energy-dispersive powder diffraction facility [1][2]. Software for the analysis of energy-dispersive powder diffraction data as been collected together to enable users to get on with analysing their data. This software has been written by Daresbury staff, users and others and covers most of the requirements of the energy-dispersive powder diffraction community. This is not however intended to be a finished program package. Such a package is under development as part of the Powder Diffraction Program Library (PDPL) and will eventually replace the existing programs. This document describes the software that is currently available where ever possible referring to PDPL programs. Programs that have been described elsewhere are referenced and only information essential to running the programs is included here. I hope that this document will enable users of the energy-dispersive powder diffraction facility to get on with analysing their data with as little need of supervision as possible.

2 Arrangement of computers and programs

EDPD data analysis programs are avalible on Daresbury Laboratory Vax A (DLVA), and on micro-Vaxes on stations 9.1 (pod1) and 9.7 (int9). Most users collect their EDPD data on station 9.7 where it is temporarily stored until it is transferred to the SRS database. Data can be retrieved from the database by any of the Vaxes by using the TFILE program [2]. The software is set up in an identical manner on all three of the Vaxes. The only difference between DLVA and the micro-Vaxes is that users have personal ids on DLVA but only shared ids on the micro-Vaxes.

If you have an account on DLVA then the following lines must be included in your login.com file:

@user1:[int9dl.commands]edsprogs

and:

@user1:[ckb.pdpl]pdpl

These lines link you into the **EDPD** and **PDPL** programs, individual programs may then be run by simply typing the program name. **SRS** programs are run by typing SRD followed by the program name, SRD GENIE, for example.

Some programs produce graphical output in a file. These files are called grid files and may be sent to a hard copy device by using the view command. Grid files always end with the extension .GRD. To view a grid file on the laser printer type:

view grid gridfilename.grd lzr2665 all

and on the Hewlett-Packard pen plotter:

view grid gridfilename.grd hp7550 all

3 Energy-dispersive powder diffraction data analysis software

These programs have been collected from a number of sources. I am very grateful to all the people who have contributed to this collection and I hope that we can share even more of our software in this manner in the future.

3.1 Graphics

There are three main graphics programs used by the powder diffraction community. These programs were independently written at different institutions and complement each other. Most people use all three programs for different things.

3.1.1 Genie

GENIE was written at the Rutherford Appleton Laboratory [3] for the analysis of neutron scattering data. The GENIE program has a number of work spaces, into which spectra can be read, and a graphics work space into which spectra are loaded before display on the screen. Some important commands are:

Display W1 This plots the contents of workspace 1 onto the screen. It is necessary to press return to go back from the graphics display to command input.

Display W1 10 60 This displays the contents of workspace 1 from 10 to 60 x-axis units.

Cursor Once a workspace has been plotted on the screen it is sometimes useful to be able to mark off points, from example, peak positions. The cursor command puts a cursor on the screen, this can be moved around using the cursor arrows. Pressing the following keys then writes specific information to the screen:

X x-coordinates of the current cursor position.

Y y-coordinates of the current cursor position.

E returns to command mode.

Keep/Hardcopy This command writes the contents of the graphics buffer to a file called HLASER.DAT which can then be sent to the laser printer on station 9.7 by using the LASER command.

Show Assignments Shows which files have been read into which workspaces.

Help This command starts the GENIE help facility which gives information on all of the GENIE commands.

Exit This command is used to exit from the GENIE program.

A number of extra commands have been added to GENIE to aid the analysis of EDPD data:

Getmca This command is used to read MCA data sets into the GENIE program. The workspace into which the data are to be read is asked for then the name of the data file.

Getmcacal This command works in exactly the same way as the GETMCA command except that the data are converted from channels to energy using the parameters in the file calib.dat that is produced by CALMCA.

Getsrs This command reads SRS data into GENIE.

Easyread This command is used to read two column xy data into GENIE. It doesn't allow any headers or footers and is the easiest way of getting data into GENIE.

Wrtmca This command is used to write out a file in SRS MCA format.

Wrtxy This command is used to write out a file in SRS XY format.

Wrtsrs This command is used to write out files in SRS format.

Ngaus This command is used to fit a number of gaussian peaks to a region of an energy-dispersive powder diffraction pattern. First a workspace, or a portion of a workspace, must be displayed on the screen. The NGAUS command is given and the cursor is displayed on top of the displayed workspace. A range of points to be fitted is selected by moving the cursor first to the leftmost point and pressing L, and then to the rightmost point and pressing R. The program then asks for the number of peaks to be fitted and the

approximate position of each of the peak centroids. These peaks are then fitted with gaussian profiles and the fit is displayed on the screen. Pressing return takes you back to command mode where the peak fit parameters are displayed. These parameters include the peak positions, full width half maxima and areas.

Cngaus This program is exactly the same as NGAUS except that the peak positions are restrained to the input values. This program is sometimes useful when it is otherwise difficult to get a good fit.

People who define their own genie_init file may include the Daresbury symbols by putting the line:

@dir$genie:dl_symbols

at the end of their file.
Genie is run by typing SRD GENIE.

3.1.2 Plot

The plot program is part of PDPL. It is particularly useful when viewing spectra produced by other PDPL programs, for example Lazy-Pulverix. The program prompts for terminal type and then for the name of input data files. It then asks for their type, this will usually be mca or free. Full instructions can be obtained by typing m.
Plot is run by typing PLOT.

3.1.3 Plotek

Plotek was written by and is supported by the data acquisition group at Daresbury Laboratory. It is particularly useful for obtaining hardcopy of spectra. When the program starts it displays a menu. To read a file in to PLOTEK type read and then answer the questions. MCA data files usually have their data in columns 1 to 8. To display a spectrum type plot and then answer the questions. Full on line help is available in PLOTEK.
Plotek is run by typing SRD PLOTEK.

3.2 Simulation

There are three energy-dispersive powder diffraction pattern simulation programs available: Dragon, Lazy-Pulverix and ENDIX. They are of three levels of complexity: Dragon takes unit cell, space group and diffraction angle information and produces a list of hkl's and energies, Lazy-Pulverix requires full structural information and produces hkl's energies and intensities and ENDIX takes full structural information and information on the experimental conditions and produces a full diffraction pattern.

3.2.1 Dragon

Dragon was originally written by Jeremy Cockcroft at the I.L.L. and was updated for energy-dispersive calculations by A. Murray as part of the PDPL. The program first asks whether you require an energy-dispersive or monochromatic simulation. After answering energy-dispersive it asks if you require a Rietveld input data set, answer no. Next it asks how many datasets you want answer 1. The program then asks for a title, the cell constants, detector angle, maximum energy to calculate up to and the space group. The program then writes a list of Miller indices, multiplicities, d-values and energies to the terminal.

Dragon is run by typing DRAGON.

3.2.2 Lazy-Pulverix

Lazy-pulverix is part of the PDPL. It can be run with an input data file or interactively. When run interactively the program asks for a title, detector angle, energy range, cell parameters, space group and atomic information (atom types, positions, occupancies and thermal parameters). The following is an example input file:

```
TITLE Si 9.885deg two-theta
CONDIT            9.89  0.0100.0    OED N
CELL          5.43106 5.43106 5.43106 90.00000 90.00000 90.00000
SPCGRP F D 3 M
ATOM   SI     0.12500 0.12500 0.12500 0.0001.000
END
FINISH
```

This file is fixed format; OED N specifies energy-dispersive. The program produces an output data file called lazypulv.lis, containing peak positions and intensities, and a file called fout.dat. Fout.dat can be converted into a plot file, that can be displayed using PLOT, with the PDPL program DATGEN.

Lazy-Pulverix is run by typing LAZY.

3.2.3 Endix

This program [4] was written to compleatly simulate energy-dispersive powder diffraction paterns both in the laboratory and at HASYLAB. We have updated some of the input data files to include SRS conditions. The following file simulates the spectrum of Silicon for station 9.7 with an air path length of 750mm:

```
TITLE  Si, Ge, 9.885deg, synchrotron, 2.00 GeV, 750mm air
CONDIT GE SD   SY 4.75  4.9  0.500  0.5  5.0   80.0  1.0  0.0   75.  3
CRYSTL F D -3 M   5.431  0.0  0.0    0.0 0.0   0.0
ATOM   SI    1 0.125   0.125   0.125 0.  0.
END
FINISH
```

The CRYSTL card contains the space group and unit cell information. The ATOM card is similar to the ATOM cards in Lazy-pulverix.

Endix is run by typing SRD ENDIX.

3.3 MCA calibration

The first part of any energy-dispersive powder diffraction data analysis involves MCA calibration. This is done my determining the position in channels of a number of fluorescence lines of known energy. A function is then found which relates channels to energy. This function is usually linear.

3.3.1 Calmca

This program first asks for a title then the order of the fit. An input file may then be specified or data may be input from the keyboard. If the latter option is taken the program asks for the position and the error in the position of each fluorescence line used in the calibration. A zero may be input for any value that is not available. These values are then output to a file suitable for input to CALMCA on a subsequent run. Once the data is read in the program a curve of the order specified. A graph of the fit is plotted on the terminal and a grid file, called CALMCA.GRD is made with the plot in. The program also writes the calibration parameters to a file called calib.dat. This file is used by getmcacal and the values can also be used in PLOTEK and PLOT for converting data between channels and energy.

Calmca is run by typing CALMCA.

3.3.2 Quickcal

This program was written by Daniel Hausermann from Birkbeck College. It asks for an input data file in which it expects to find peaks from all of the elements in the variable energy X-ray source that is used for MCA calibration. It then finds all of these peaks, measures their positions and determines the calibration parameters in a similar manner to CALMCA. The great advantage of this program is that it is compleatly automatic and saves about an hour of effort, the only disadvantage is that sometimes the data are not collected very well and it does not work.

Quickcal is run by typing QUICKCAL.

3.4 Detector angle calibration

The second part to energy-dispersive powder diffraction data analysis is usually detector angle determination. This is done by collecting a spectrum from a standard of known unit cell parameters and then determining the angle by a linear least squares fit.

3.4.1 Calang

The program asks for a title and the name of an input file. The input file contains corresponding values of d-spacing and the measured position of lines of the calibrating material as a free format xy file. A graph of energy versus inverse d-spacing is plotted on the terminal together with the determined value of the diffraction angle. The program waits until return is pressed and then writes out a grid file called CALANG.GRD with the plot in it.

Calang is run by typing CALANG.

3.4.2 Refcel

This program is part of the PDPL. It has recently become available and will refine either the diffraction angle given a known unit cell or a unit cell given a known diffraction angle. It starts by asking for an input data file or return for terminal input. If terminal input is selected it then asks for the cell type (press return for a list), and then whether the data is monochromatic or energy-dispersive. When energy-dispersive is chosen the program asks: for the unit cell parameters, for the detector angle, whether to refine the unit cell parameters of detector angle and for a file containing a list of reflections. If you don't have a reflection file then reflections can be entered interactively as a list of Miller indices, energies and errors. The following is an example input file:

```
NH4C1 SSC
1
3.8756 3.8756 3.8756 90.0 90.0 90.0
7.142
1 0 0 25.640   0.002
1 1 0 36.2408  0.0006
1 1 1 44.34    0.03
2 0 0 51.309   0.003
2 1 0 57.416   0.008
2 1 1 62.844   0.006
```

The program prints the refined unit cell and any reflections which seem to be badly in error to the terminal.

Refcel is run by typing REFCEL.

3.5 Whole pattern fitting

Determining peak parameters by using programs like NGAUS in GENIE is very tedious and time consuming. The following programs attempt to measure these parameters with some degree of automation.

3.5.1 Pkfind

This program was written by A.J. Norman of Leicester University. It takes a spectrum, smooths it then uses first and second derivative methods to find peaks before fitting them with gaussian functions. The program asks for the name of the input data file then asks what type of smoothing is required. It then asks for five file names for: the original spectrum, the smooth spectrum, the first derivatives, second derivatives and peak positions to be written to. The program determines peak positions, in channels, and peak areas.

PKFIND is run by typing PKFIND.

3.5.2 Gamanal

The GAMANAL program was written at AERE Harwell by Mrs J.A.B. Goodall for the analysis of Gamma-ray spectra [5]. The program first takes a standard spectrum and determines shape parameters based on a number of selected peaks, subsequent spectra can then be analysed using these parameters to yield peak positions, areas and full widths. The program seems to work extremely well with good data but can sometimes be completely impossible. Nevertheless it is a totally automatic program. The program is run by typing SRD GAMANAL.

All input files for GAMANAL consist of lines of format (A8,2X,7E10.0), the first parameter is a code word followed by up to seven values, for example the following file was used to determine shape parameters from a spectrum collected from NBS Silicon 640b:

```
TITLE
OBTAIN PEAK SHAPE PARAMETERS FROM NBS SI STANDARD
DATAIN    17194.    1200.    1200.             0.      1.      8.
ENIN       2.7866   .02819
SHAPEDO       5.      1.
        714.0   22.84
       1229.0   37.44
       1458.0   43.91
       1780.0   52.98
       1948.0   57.72
PEAKPLOT      0.
PROCESS     600.    2100.
GRAPH         1.      0.
STOP
```

The first code word is TITLE, this code word takes no values but tells the program to expect a title on the next line. The second code word is DATAIN, this has: the run number, the live time, the real time, a blank record, the number of lines to skip, the first column for data in the input file and the last column for data in the input file as values. The ENIN card has the energy calibration values from CALMCA or QUICKCAL. The SHAPEDO card takes two values the first specifies how many peaks

are to be fitted in order to determine the peak shape parameters, the second specifies which peak shape parameters are to be refined: a value of 1 refines parameters 1 and 2, a value of 2 refines parameters 1 to 4, a value of 3 refines parameters 1 to 5, and a value of 4 refines parameters 1 to 6. The positions in channels and energy of each of the peaks to be fitted is then given. The PEAKPLOT card with a value of zero suppresses a line printer plot. The PROCESS card initiates calculations and prints out the results. It takes two values: the first and last channels to be processed. The GRAPH card has values for the for the first channel to be plotted and a switch which is zero for the spectrum to be plotted against channels and one for the spectrum to be plotted against energy. The last card STOP halts program execution.

The peak shape parameters determined using the above input file were:

s1	-0.002
s2	$0.377 \cdot 10^{-2}$
s3	-6.88
s4	0.0721
s5	1.2
s6	0.4

Once peak shape parameters have been determined spectra can be analysed automatically using GAMANAL. The following file was used to analyse the silicon spectrum using the shape parameters determined above:

```
TITLE
SI NBS STANDARD
DATAIN     17194.     889.     889.              0.     1.     8.
ENIN       2.7866     .02819
SHAPEIN    -0.002   0.00377   -6.88   0.0721    1.2    0.4
PEAKPLOT   0.
PROCESS    600.     3500.
GRAPH      1.        0.
STOP
```

This file is the same as the one used for peak shape parameter determination except that it has the SHAPEIN card instead of the SHAPEDO card.

Gamanal is run by typing GAMANAL.

3.6 Unit cell refinement

Often energy-dispersive powder diffraction is used for unit cell determinations; usually at high pressure. The following programs can be used to determine unit cell parameters from energy-dispersive powder diffraction data using least squares fitting.

3.6.1 Ecel

This program is used for refining unit cell parameters. The program asks for an input file or you can press return for terminal input. The program requires a title, a cell type (1-cubic, 2-rhombohedral, 3-hexagonal, 4-tetragonal, 5-orthorhombic, 6-monoclinic, 7-triclinic), a starting set of unit cell parameters, the diffraction angle and a list of Miller indices with energies and errors. The following is an example file:

```
NH4C1 55C
1
3.8756 3.8756 3.8756 90.0 90.0 90.0
7.142
1 0 0 25.640    0.002
1 1 0 36.2408   0.0006
1 1 1 44.34     0.03
2 0 0 51.309    0.003
2 1 0 57.416    0.008
2 1 1 62.844    0.006
```

The program refines the unit cell and prints out the refined value together with the deviation of the observed peak positions from the calculated peak positions.

Ecel is run by typing ECEL.

3.6.2 Refcel

This program is part of the PDPL. It has recently become available and will refine either the diffraction angle given a known unit cell or a unit cell given a known diffraction angle. It starts by asking for an input data file or return for terminal input. If terminal input is selected it then asks for the cell type (press return for a list), and then whether the data is monochromatic or energy-dispersive. When energy-dispersive is chosen the program asks: for the unit cell parameters, for the detector angle, whether to refine the unit cell parameters of detector angle and for a file containing a list of reflections. If you don't have a reflection file then reflections can be entered interactively as a list of Miller indices, energies and errors. The following is an example input file:

```
NH4C1 55C
1
3.8756 3.8756 3.8756 90.0 90.0 90.0
7.142
1 0 0 25.640    0.002
1 1 0 36.2408   0.0006
1 1 1 44.34     0.03
2 0 0 51.309    0.003
2 1 0 57.416    0.008
2 1 1 62.844    0.006
```

The program prints the refined detector angle and any reflections which seem to be badly in error to the terminal.

Refcel is run by typing REFCEL.

4 Analysis of kinetic data

The initial analysis of kinetic data involves extract of peak parameters and determination of the degree transformed. Subsequent analysis can be carried out with the following programs.

4.1 Simulation

4.1.1 Avsim

This program simulates a S-curve, given values of the activation energy and rate constant, using Avrami's equation. The program first asks the rate, the order, the time step, the error in the time zero point and an output filename. The program produces a xy file, of the time and degree of transformation, which can be displayed using PLOTEK or GENIE.

Avsim is run by typing AVSIM.

4.2 Fitting data to rate laws

4.2.1 Avfit

This program fits Avrami's equation to an input xy data file. It asks for: the input data filename, an output filename, a plot filename, a title, starting values for the rate and order and refinement keys for the rate and order (zero - don't refine, one - refine). The program produces a three column file containing x, y and ycalc.

Avfit is run by typing AVFIT.

4.2.2 Exp

This program fits an exponential function to an input xy data file. It asks for: the input data filename, an output filename, a plot filename, a title, starting values for the rate and order and refinement keys for the rate and order (zero - don't refine, one - refine). The program produces a three column file containing x, y and ycalc.

Exp is run by typing EXP.

4.2.3 Hyper

This program fits an hyperbolic function to an input xy data file. It asks for: the input data filename, an output filename, a plot filename, a title, starting values for the rate and order and refinement keys for the rate and

order (zero - don't refine, one - refine). The program produces a three column file containing x, y and ycalc.

Hyper is run by typing HYPER.

4.2.4 Power

This program fits a power law to an input xy data file. It asks for: the input data filename, an output filename, a plot filename, a title, starting values for the rate and order and refinement keys for the rate and order (zero - don't refine, one - refine). The program produces a three column file containing x, y and ycalc.

Power is run by typing POWER.

4.3 Other useful programs

4.3.1 Rescale

This program is used to rescale experimentally determined S-curves from arbitrary intensity units to the interval between zero and one. The program asks for an input data file, in XY format, and an output file name. It then asks for a top and bottom value, to scale to one and zero, and a start and end value, which can be used to select a section of the data. Finally the program asks whether the data should be inverted or not. Data are usually rescaled to go from zero to one.

Rescale is run by typing RESCALE.

4.3.2 Linfit

This program fits a straight line to a set of data. It asks for an input file and an output file, reads in the data, fits a straight line and writes out a three column file containing x, y, and ycalc. This file can then be displayed using PLOTEK or GENIE.

Linfit is run by typing LINFIT.

4.3.3 Lnlnfit

This program converts a set of data ready for a ln-ln plot, fits a straight line to the converted data and writes out a three column file which can be displayed using PLOTEK or GENIE.

Lnlnfit is run by typing LNLNFIT.

4.3.4 Lnlnlnfit

This program converts a set of data ready for a lnln-ln plot, fits a straight line to the converted data and writes out a three column file which can be displayed using PLOTEK or GENIE.

Lnlnlnfit is run by typing LNLNLNFIT.

5 Analysis of high pressure data

5.1 Pressure calibration

We do not have many programs for the analysis of pressure data yet but I hope that this section will grow very rapidly over the next few months.

5.1.1 Presscalc

This program was written by A. Deacon at Daresbury Laboratory. It calculates the pressure inside a pressure cell from the a parameter of NaCl using the data of Decker [6] and five point interpolation. The program asks for a value of a and returns the appropriate pressure.

The program is run by typing PRESSCALC.

References

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