

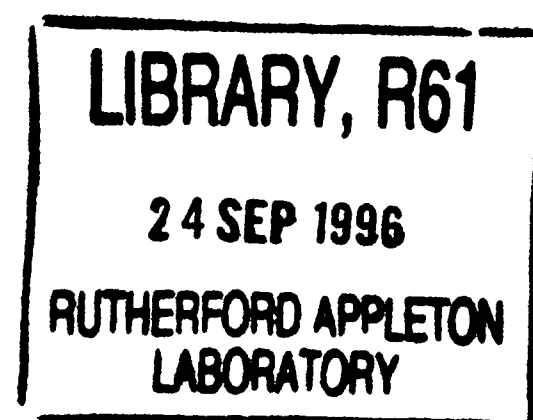
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eVS Analysis Routines for Fitting Time of Flight Data

J Mayers



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eVS Analysis Routines for Fitting Time of Flight Data

J. Mayers

Programs for Fitting eVS Data in Time of Flight

1. Introduction

This report gives details of analysis programs which are available for directly fitting eVS time of flight data. Time of flight data from samples containing a number of different masses can be fitted directly using the command >TFIT_FSE. A sample containing N different masses will produce N peaks in the time of flight spectrum. It is assumed in the analysis that each peak can be characterised by three parameters;

(1) the standard deviation σ_i of the (assumed) Gaussian momentum distribution corresponding to mass i . This can either be set at a fixed value, or used as a fitting parameter. In isotropic samples σ_i is related in a simple way to the mean kinetic energy of the atoms (see equation A1.7)

(2) The peak area A_i . The area A_i can be related to the product of the concentration and the scattering cross-section for atomic mass i . It can be fixed, if the sample composition is known or included as a fitting parameter. In the latter case the fitted values of the A_i can be used to determine the sample composition.

(3) The peak position. This can be accurately calculated from the atomic mass and is always fixed by the value of mass which is input to the program.

There are therefore only two free parameters defining each peak. For peak i these are the area A_i and σ_i , the r.m.s momentum of the atom. Thus for a sample containing N different masses there are $2N$ fitting parameters for each time of flight spectrum.

The output of the program is a file which contains the values of σ_i and A_i , for each time of flight spectrum and for each atomic mass. This file can be examined and analysed using further programs, to determine the sample concentration and the atomic kinetic energies of each atomic mass present. For single crystal samples the r.m.s atomic momentum can be determined along different crystalline symmetry directions.

The principles behind the data analysis are given in Appendix 1. Sections 2 and 3 of this guide tell you how to run the programs and analyse the program output for samples with no preferred orientation, i.e. powders, liquids, glasses etc. Section 4 provides further information on how to analyse single crystal data.

2. The >TFIT_FSE Program

The command file used to run the fitting programs in time of flight is listed in appendix 2. It is suggested that after an initial use of the program interactively (in order to familiarise yourself with the program), the TFIT_FSE program should be run in batch mode since;

- (a) It takes some time (~10-20 minutes) to run
- (b) Once a command file for one run has been created, it can be easily modified (usually by changing only the run number) to process other runs. As well as saving labour, this also ensures that all runs are processed in the same way. This is important if you are looking for systematic changes with e.g. temperature, composition, pressure, sample angle etc
- (c) The batch job will produce a log file which can be examined for errors etc.

A command file can be written and submitted to the batch queue by the command \$ @SUBMIT. You will be prompted for a queue number. Numbers 1 and 3 are usually good. (To find the status of the queue, type \$QU).

Note that the program uses a fast Fourier transform routine to incorporate the instrument resolution function. **This routine will fail if the number of points in the data set contains a prime factor greater than 19 and will give the error message "IFAIL=1".** It is suggested that the data set is rebinned so that the number of data points is a power of 2 (eg 64, 128, 256 or 512 points). This can be done in Genie using the >REB command (see the example command file below). **The bin size should be a multiple of 0.25 μ sec,** otherwise spurious shifts in the peak position will be produced by the >REB command.

As an example to illustrate the programs, a data set from a 50% mixture of H₂O and D₂O is used. The command file run in batch to process the H₂O/D₂O data is listed below, with comments in italics. The comments should be omitted in a real file. The input to the >TFIT_FSE routine should be compared with the program description in Appendix 2.

Example Command File HDO3467T.com

\$ USER	<i>Specifies directory for program output.</i>
\$ GENIE	<i>Opens Genie package</i>
\$ DIFF	<i>Takes difference between foil in and foil out data</i>
3467	<i>Run number</i>
1	<i>First spectrum</i>
32	<i>Last spectrum. Spectra 1-32 are processed in this command file.</i>
>REB	<i>Rebins data to give no of data pts which is power of 2.</i>
1	<i>First spectrum</i>
32	<i>Last spectrum</i>
30	<i>Lower limit for binning</i>

540 *Upper limit for binning*
2 *Bin width. There are $(540-30)/2+1=256$ data points*
>GWRITE *Writes data into Genie files.*
HDO3467T *Name of Genie data file.*
1 *First spectrum*
32 *Last spectrum*
>TFIT_FSE *Runs time of flight fitting programs*
HDO3467T *Name of data file containing output. HDO3469T.DAT will be created.*
 The program also creates GENIE files containing the fits to individual
 spectra. These have the names HDO3467T_FIT.1, HDO3467T_FIT.2 etc.
 The name inserted here should be the same as that used in the previous
 >GWRITE command.
1 *First spectrum*
32 *Last spectrum*
4912 *Analysis energy (obtained from calibration)*
135 *Energy resolution (obtained from calibration)*
3455 *Number of instrument parameter file.*
0 *No linear background is included in the fit*
3 *Number of masses in the sample.*
1.0079 *Mass 1 (H)*
81 *Product of bound cross-section and no of atoms (i.e $81 \times 0.5 \times 2$)*
0 *Width of H peak is fitted*
2.015 *Mass 2 (D)*
7.63 *Product of bound cross-section and no of atoms (i.e $7.63 \times 0.5 \times 2$)*
0 *Width of D peak is fitted.*
16 *Mass 3 (O)*
4.234 *Product of bound cross-section and no of atoms (i.e 4.234×1)*
0
> EX

- Note that 256 points have been chosen in the rebin command. It is suggested that the bin width is chosen as a multiple of 0.25, the grid over which the raw data is collected. Otherwise the GENIE rebin command can produce spurious shifts in the peak positions.
- It was assumed that the concentration of the mixture was 50% H₂O and 50% D₂O. Thus the area of e.g. the hydrogen peak should be 81 (bound cross section)*2(number of atoms)*0.5 (relative concentration of H₂O)=81. Using a non-zero value as input for the product of cross-section and number of atoms fixes this parameter. If zero is entered at this point, the area will be included as a fitting parameter.
- It is suggested that all files are given the same name. The example above used the name HDO3467T. Thus HDO is a mnemonic for the sample, 3467 denotes the run number and T specifies that analysis is in time of flight (other routines can be used

to analyse in atomic momentum space). Thus the command file is HDO3467T.COM, the GENIE files produced have names HDO3467T.1 , HDO3467T_FIT.1 etc and the data file produced by the TFIT program has the name HDO3467T.DAT. Note that the same name for output files must be given in the >GDATA and TFIT_FSE routines.

- The @SUBMIT command will produce a log file HDO3467T.LOG in the directory from which you submitted the command file. This is very useful for diagnostic purposes, particularly when you are first creating a command file.
- It is suggested that when the command file is first created it is tested and debugged by running on a single detector, rather than 1-32.

3. Examination of Output

The command file above produced a GENIE data file for each spectrum, together with a fit to the data. The data file name is specified in the >GWRITE command as HDO3467T and these files will be of the form . HDO3467T.1, HDO3467T.2.....HDO3467T.32. The fit file name is specified in the TFIT_FSE routine as HDO3467T (note this must be the same name as in the >GWRITE routine) and will produce the fit files HDO3467T_FIT.1, HDO3467T_FIT.2 etc.

3a. Examination of GENIE Files

The data and fit can be examined by use of the commands >FITREAD and >FITPLOT in GENIE. The former reads in the data files and fits from the created GENIE files. The latter plots data and fit. An example of how to use these programs is given below. Prompts are written in normal type and replies to the prompts in bold.

>FITREAD

```
> FILENAME      HDO3467T
> First Spectrum 1
> Last Spectrum 32
```

The responses are for the output of the file HDO3467T. The program reads in the files HDO3467.n which were created by the >GWRITE routine the the example command file above and the files HDO3467T_FIT.n which were created by the >TFIT_FSE routine. The index n runs from 1 to 32.

>FITPLOT

```
> Lower limit?      100
> Upper limit ?     500
> Plot E or M?      E
> Bin width?        2
> Spectrum number?  9
```

The above series of responses and replies would plot points in the time of flight spectrum of detector number 9, as error bars, with the fit to the data shown as a solid line. The data and fit will be plotted between 100 and 500 μ seconds with a time bin width of 2 μ sec. The

INSTRUMENT: EVS	USER: AKS/pzz
RUN NUMBER: 3467	RUN START TIME: 28-OCT-1995 22:50:56
SPECTRUM : 39	PLOT DATE: Mon 24-JUN-1996 15:10:34
	BINNING IN GROUPS OF 2
LOCATION: EVS\$DUA0:[EVSMGR.DATA]EVS03467.RAW	

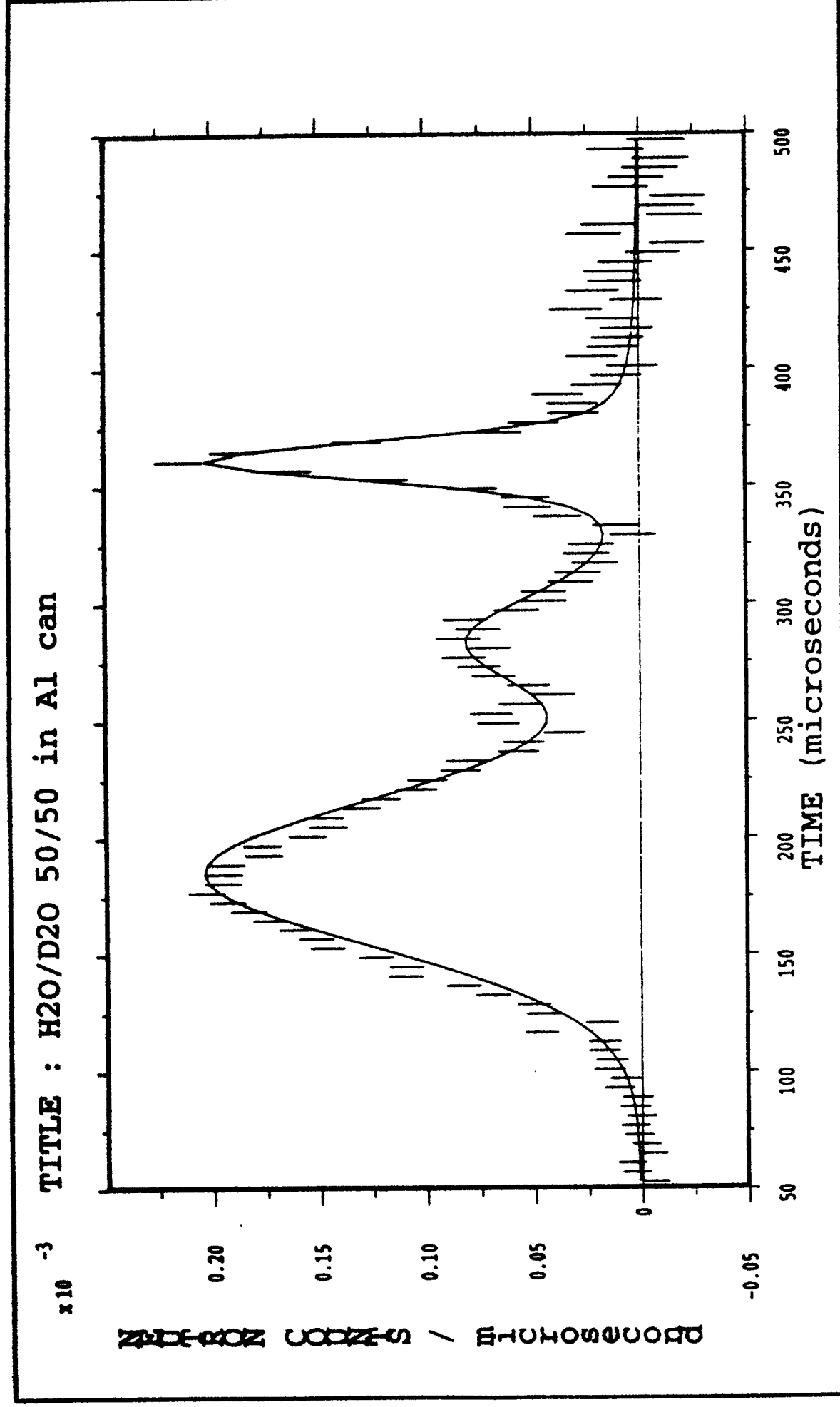


Figure 1. Time of flight data from example data. The solid line is the fit produced by >TFIT_FSE. The peak centred at ~ 190 μsec corresponds to scattering from hydrogen, that at ~290 μsec from deuterium and that at ~370 μsec from oxygen.

plot produced on the screen in this case is shown in figure 1. The program will continue to prompt you for a spectrum number. To exit the routine press the ctrl and y keys simultaneously.

Visual examination of the data and fit is very important as it is usually immediately obvious to the eye if there are any serious problems in the fitting. When you have examined all spectra and made a note of all detectors where there appears to be a problem with either data or fit and obtained any hard copy you require, it is recommended that the raw data and fit files are deleted since they take up a lot of disk space. Hard copy of any GENIE plots can be obtained using the >LAS command.

3b. Examination of Data Files

The TFFT_FSE routine also produces a data file which contains all the fitted parameters with errors. This can be examined by the command \$TPROC. Note that this must be run outside GENIE. To exit GENIE, while still retaining any data you have created in workspaces type >j/p. To return to genie type \$LOG. (NB '>' denotes command in GENIE, '\$' denotes command outside GENIE).

The TPROC routine allows you to examine the set of values from the whole range of detectors to check for internal consistency and whether any detectors are giving consistently unreliable results (e.g. due to electronics problems). Mean values of widths and areas of peaks from different atomic masses can be calculated and detectors which can be identified as giving incorrect values can be eliminated. An example of how to use this routine is given below. Prompts from the program are written in normal type, your replies in bold type. Comments (which will not appear when you are running the program) appear in italics.

\$ TPROC

Name of file containing output of TFFT routines?

HDO3467T *The name of the data file*

Number of masses= **3**

Number of detectors= **32**

The file contains data on the following masses.

1 **M=1.0079** *List of different masses in the data file*

2 **M=2.0150**

3 **M=16.000**

Examine the data on peak areas (1) or widths (2)?

Either areas or widths of peaks from different masses can be examined.

Type 0 to exit program

1 *Examine peak areas*

Mass number?

1

Peak number 1 Mass=1.0079

Arrange in order of increasing angle (y=1,n=0)

HDO3467T M=1.0079 Area Values

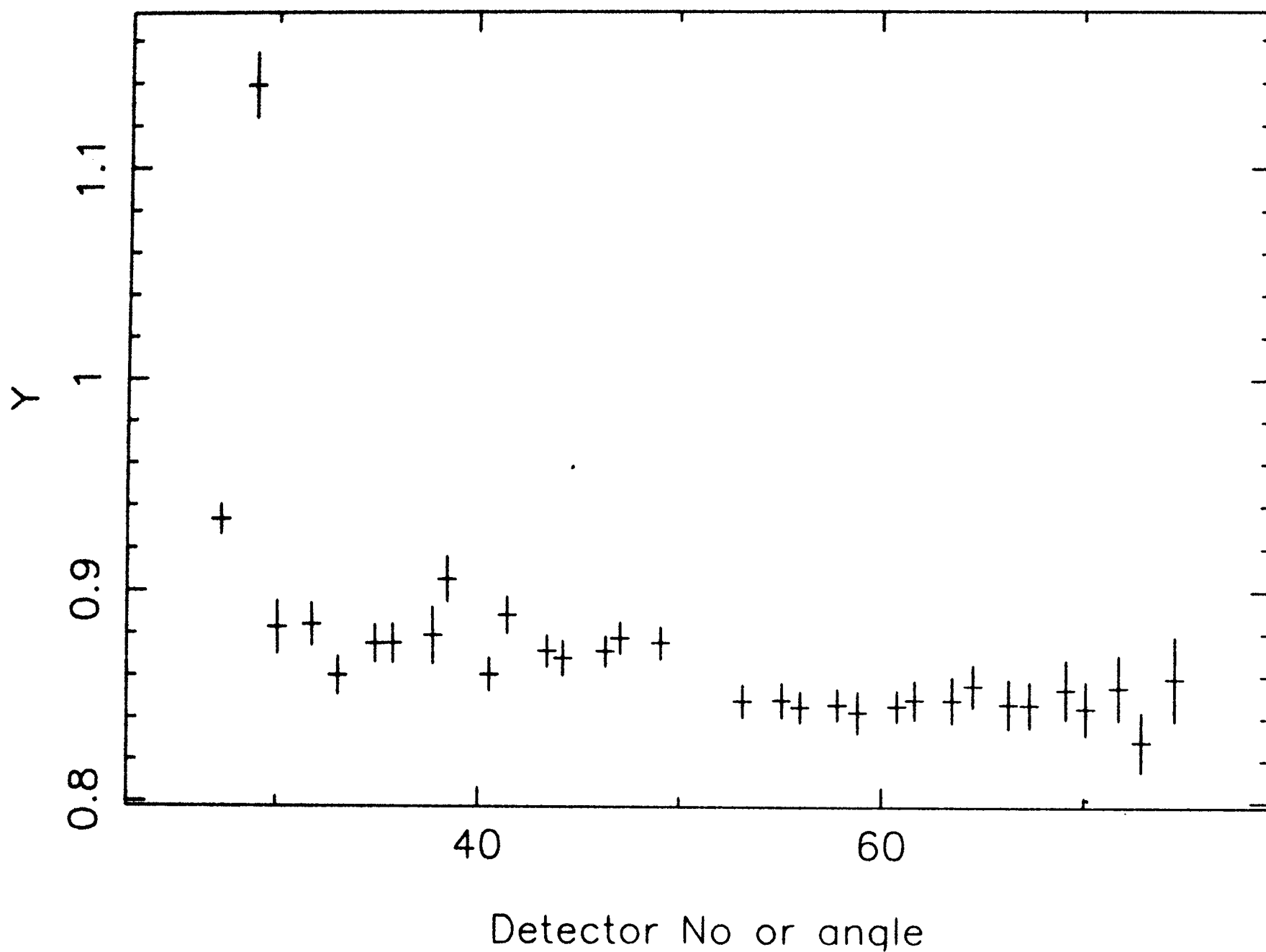


Figure 2. Plot produced by \$TPROC. In this case areas of the H peak are plotted as a function of scattering angle. Note that detectors 1 and 2 are producing obviously anomalous values and have been eliminated before the calculation of mean values.

The data in the file can be examined either as a function of detector number (this is useful for determining which detectors are giving spurious results) or as a function of scattering angle. (This could give an indication of whether there are any systematic errors. e.g. a consistent trend in the size of peaks area or width as a function of scattering angle)

1

Enter number of instrument parameter file

3455

The angle corresponding to a particular detector is read from this file. If plotting as a function of detector number you are not asked for the IP number.

Plot area values (y=1,n=0)

1

Enter title of plot

HDO3467T M=1.0079 Area Values

Whatever you type here will appear as a header in the plot.

Graphics device/type (? to see list)

/x *For a plot on the screen type /x. For a postscript file type /PS.*

Change limits? (Y=1,N=0)

1

Current values are

XMIN=22.621

XMAX=79.17

YMIN=0.7976

YMAX=1.1731

ENTER NEW VALUES OF XMIN XMAX

/

ENTER NEW VALUES OF YMIN, YMAX

/

Graphics device/type (? to see list)

/PS

You can replot with specified limits. If you type /, the limits will not be changed. Thus you can produce a postscript file by typing 1 in response to the prompt "Change limits?" then / in response to the request for new limits, followed by /PS when asked for the device type. This will produce a PGPLOT.PS file which will produce hard copy of what you have just seen on the terminal screen. The postscript file can be turned into hard copy by the command \$PPS. You will be prompted for the number of the laser printer. e.g. 3 will produce output on laser printer 3 in the LAD instrument cabin. To produce output on a different laser printer, change 3 to a different number. The different printers and locations are;

0. *First floor of R3 1.37*

1. *Top Floor of R3 2.25*

2. *R55 DAC*

3. *R55 LAD*

The plot produced by this sequence of responses is shown in figure 2

CHANGE LIMITS? (y=1,n=0)

0

NUMBER OF DETECTOR TO BE EXCLUDED (0 TO END)

2

NUMBER OF DETECTOR TO BE EXCLUDED (0 TO END)

1

NUMBER OF DETECTOR TO BE EXCLUDED (0 TO END)

0

It may be apparent from the plot (or from examination of the data and fit files (using >FREAD and >FPLOT) that some spectra are unreliable. In the above case detectors 1 and 2 were producing unreliable results and were excluded from any calculation of average values. The procedure of excluding detectors should be treated with caution as some values will lie outside the expected deviation from the mean due to purely statistical fluctuations. Only exclude a detector if you are sure it is producing unreliable results, e.g. if it gives anomalous results in every run or if visual observation of the fit shows that there are problems.

The following detectors are excluded from averages.

2

1

Calculate mean of area values

First and last points?

1 8

3	XV=30.097	X=0.88288	+ 1.26E-02
4	XV=31.811	X=0.88421	+1.006E-02
5	XV=33.084	X=0.86024	+ 9.099E-03
6	XV=34.927	X=0.87525	+8.897E-03
7	XV=35.820	X=0.87530	+1.351E-02
8	XV=37.810	X=0.8791	+1.353E-02

WTD MEAN=0.8748 +4.155E-03

MEAN=0.8762 ST. DEV=3.53E-03

Note that detectors 1 and 2 are excluded from the average as specified by the replies to the previous command. In this case XV is the scattering angle. If you type 0 in response to the prompt "Arrange in order of increasing angle" XV would be the detector number. The wtd mean is the mean of different values, weighted by their statistical errors and the error is the statistical error of the measurement. The standard deviation from the mean is a more reliable indication of the true error, since there generally other sources of error which do not appear in the statistical error. e.g. Variation of extracted values with angle. The presence of systematic errors, in addition to statistical errors is reflected in the fact that the standard deviation from the mean is generally larger than the error on the weighted mean. Note that there is little point in getting very good statistics, if the systematic errors are dominant. This should be taken into account when you are determining the run times. (a suggested run time is one which gives a statistical error which is half that of the standard deviation from the mean)

PLOT VALUES INCLUDED IN MEAN? (Y=1,N=0)

There is an option to plot all the values included in the calculation of the mean (in this case 6 values between 30.097 and 37.81 degrees. This provides a further check on possible anomalous data points.

FIRST AND LAST POINTS

0 0

If the first and last points are the same the program returns to the first prompt. You can now examine either the areas or widths corresponding to another mass in the file.

Examine data on peak areas (1) or widths (2)

Type 0 to exit program

0

Exit program.

Determination of Sample Composition

By examination of the peak area the composition of the sample can be determined. As an example of how this is done, consider data taken from a calibration sample of polyethylene (CH₂). The peak areas derived from TPROC were

Atom	Mass	Area	Cross-section
Hydrogen	1.0079	0.960 ± 0.006	81.7 barns
Carbon	12	0.034 ± 0.004	5.56 barns

The numbers of atoms are in the ratio H=0.960/81.7 : C=0.034/5.56, i.e. 0.0118:0.0061 or 1.93:1. Within error (± 0.2) this agrees with the actual sample composition.

Note that the relevant neutron cross-sections are the bound cross-sections listed in standard tables such as those on the wall of the eVS instrument cabin.

Determination of Atomic Kinetic Energies or Equivalent Frequencies

In isotropic samples, the values of the peak widths can be converted into atomic kinetic energies by use of the command \$KE. You will be prompted for the atomic mass, the width and the error. The program calculates the atomic kinetic energy in a variety of units. It also calculates the equivalent frequency, i.e. the frequency of an isotropic harmonic oscillator at zero temperature, which would give the measured value of the peak width.

4. Single Crystal Samples

If you are running a sample with preferred orientation, or a single crystal sample, you will be interested in the variation of peak widths (and corresponding kinetic energy values) with sample orientation. In single crystals the full directional Compton profile $J(\vec{q}, y)$ can be measured as a function of the direction of \vec{q} (see Appendix 1). Data from single crystals can be further analysed for anisotropy, after fitting in time of flight. The routines described

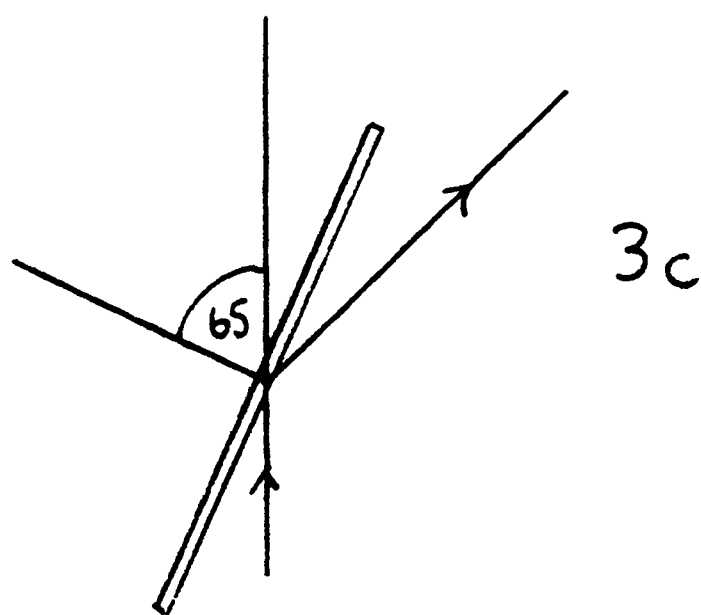
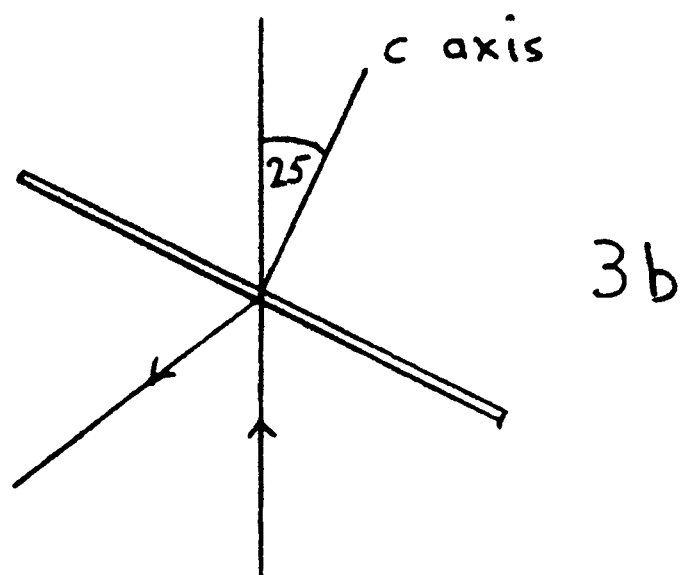
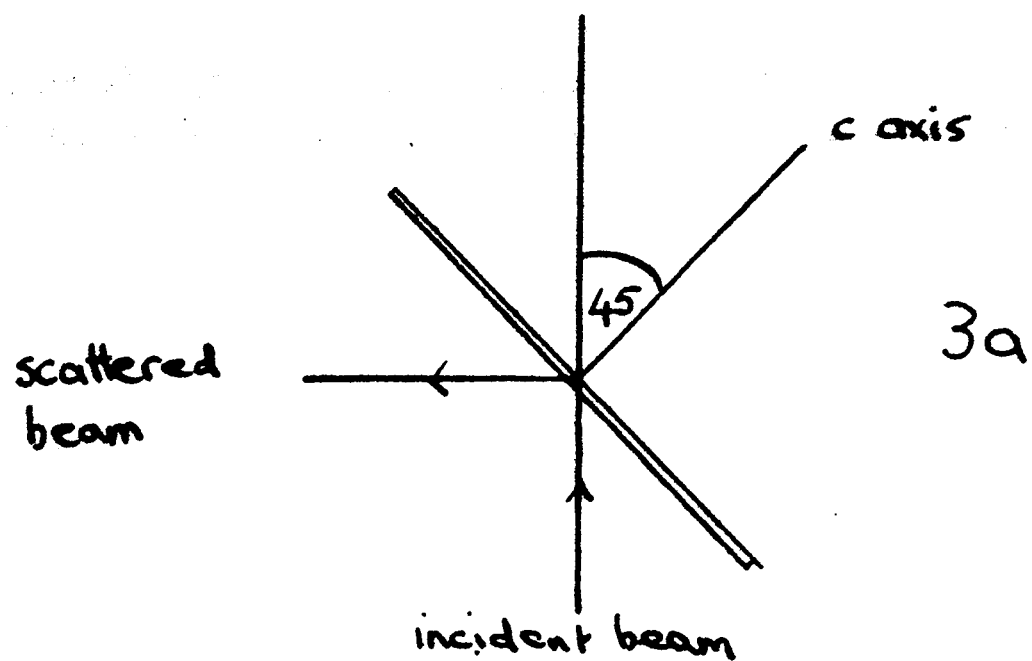


Figure 3. Experimental geometry for the three runs used in the example of section 4. The sample was graphite, with the c axis perpendicular to the sample plane. The position of the Bragg peak is determined by specular reflection from crystal planes perpendicular to the c axis as indicated in the diagrams.

in this section are suitable for analysis of masses greater than 2 (ie for all samples except those containing H and D). In single crystal experiments on H and D, the direction of \hat{q} varies significantly over the peak width and other analysis methods must be used. (see "Guide to eVS data analysis programs).

As an example of these procedures, we consider data from a sample of pyrolytic graphite which has a single preferred direction [0002] perpendicular to the hexagonal planes in the graphite structure. Three runs were performed with a slab sample with the c axis perpendicular to the slab; (a) The slab was at 45° to the beam, with the [0002] Bragg reflection appearing at a scattering angle of -87.5° (Figure 3a) (b) with the slab at an angle of 25° to the beam with the [0002] Bragg reflection at a scattering angle of -127° (Figure 3b) and (c) with the slab at 65° to the beam and the [0002] Bragg peak at a scattering angle of 50° (Figure 3c).

The orientation of the sample in the beam can be determined by examination of the time of flight spectra, which will contain Bragg peaks from the sample at long times (>2000 μ sec) It is assumed that the crystal is already aligned so that a known symmetry direction occurs somewhere in the horizontal plane. It is suggested that you choose a long d spacing Bragg peak and then rotate the sample about the vertical axis in steps of $\sim 10^\circ$ until this peak appears in one of the detectors, since it is often difficult to unambiguously assign a peak at short d spacing. The time of flight spectra can be converted to d spacing using the command >DTRANS which is described in appendix 2.

4b Creation of a Composite Data File from a Number of Runs

The first step is to analyse the data from each run as described in sections 2 and 3, to produce the files C3598.dat, C3599.dat and c3600.dat. The >FITREAD, >FITPLOT and \$TPROC programs should be used to determine which detectors are producing unreliable results. The unreliable detectors can be eliminated from the data files using the routine \$BAD_DET. In the example run detector 25 was giving significantly broader values for peak widths in all three runs. A new file C3598M.dat was created from the file C3598.dat as follows

\$ BAD_DET

Modify output files from TFFT routines to eliminate bad detectors.

ENTER FILENAME

C3598T.dat

NUMBER OF BAD DETECTOR? (0 TO END)

25

NUMBER OF BAD DETECTOR? (0 TO END)

0

Detector 25 will be deleted from new file.

Number of masses=1

Number of detectors=32
1 Atomic Mass=12.00
Create New File (Y=1,N=0)
1

Enter Filename

c3598m.dat

An identical procedure was followed for run 3599 and 3600 so that the three modified files C3598M.DAT, C3599M.DAT and C3600M.dat each containing data with detector 25 removed were created.

The files from different runs can be combined into a composite data set by the routine >ANGLEPLOT. This routine reads in the widths of a specified mass from different runs and orders the data in individual detectors and runs, according to the angle between the direction of \hat{q} and a crystalline symmetry direction. The crystalline symmetry direction is calculated from the number of the detector in which the Bragg peak, corresponding to the required direction, appears. The graphite data is used below as an example of how this program operates.

\$ANGLEPLOT

Enter number of instrument parameter file

3594

Analyser energy in meV?

4908

Enter data filename

c3598m

1 Atomic mass=12.00

Number of mass of interest

1

Number of detector containing crystal Bragg peak

29 *The [0002] Bragg peak occurred in spectrum 29 for run 3598.*

Bragg peak is at scattering angle of -87.55 deg.

Read in another data file ? (Y=1,N=0)

1

Enter data filename

c3599m

Number of detector containing crystal Bragg peak

21 *The [0002] Bragg peak occurred in spectrum 21 for run 3599.*

Bragg peak is at scattering angle of -127.100 deg.

Read in another data file ? (Y=1,N=0)

1

Enter data filename

c3600m

Number of detector containing crystal Bragg peak

14 *The [0002] Bragg peak occurred in spectrum 14 for run 3600.*

Bragg peak is at scattering angle of 49.199 deg.

Read in another data file ? (Y=1,N=0)

0

Enter title of plot *Whatever is entered here will appear as the plot header.*

Graphics device/type (? to see list)

/x *A plot of the widths as a function of angle will be shown.*

change limits? (Y=1,N=0)

0

Output to file? (Y=1,N=0)

1

Name of output file

sigma.dat

This series of commands will create a file sigma .dat with three columns. Column 1 contains the angle between \hat{q} and the crystal symmetry direction. Column 2 contains the sigma value and column 3 the error in the sigma value.

4c Fitting Single Crystal Data

The file produced by \$ANGLEPLOT can be read into a GENIE workspace by the command >LOAD as follows.

>LOAD

Enter workspace number: 1

Enter data file name **sigma.dat**

Enter X caption **Angle of q**

Enter Y caption **Sigma**

This series of commands loads the data into workspace 1. It can be plotted by the command >D W1. The x axis will have the caption " Angle of q " and the y axis " Sigma". The routine >EFIT fits an anisotropic Gaussian distribution to the data. The start values for the fit can be estimated by examination of the data (see figure 4). If 0 is entered for the angle of the primitive axis, the angle is fixed at zero. Otherwise this parameter can also be fitted. (This allows a cross check on the crystal orientation determined from the angles of Bragg reflections).

>EFIT

Number of workspace containing data	1
Start value for width along principal axis	10
Start value for width perpendicular to principal axis	12
Start value for angle of principal axis (0 to fix)	0.1

Fitted values for parameters;

Principal Axis sigma=9.9675 +- 1.19E-02

Perpendicular axis sigma=13.407 +- 1.34E-02

Angle of principal axis=4.83+-0.26

INSTRUMENT:	1	USER:	not available
RUN NUMBER:	1	RUN START TIME:	not available
SPECTRUM :	1	PLOT DATE:	Mon 24-JUN-1996 16:00
		BINNING IN GROUPS OF	2
LOCATION:	SIGMA.DAT		

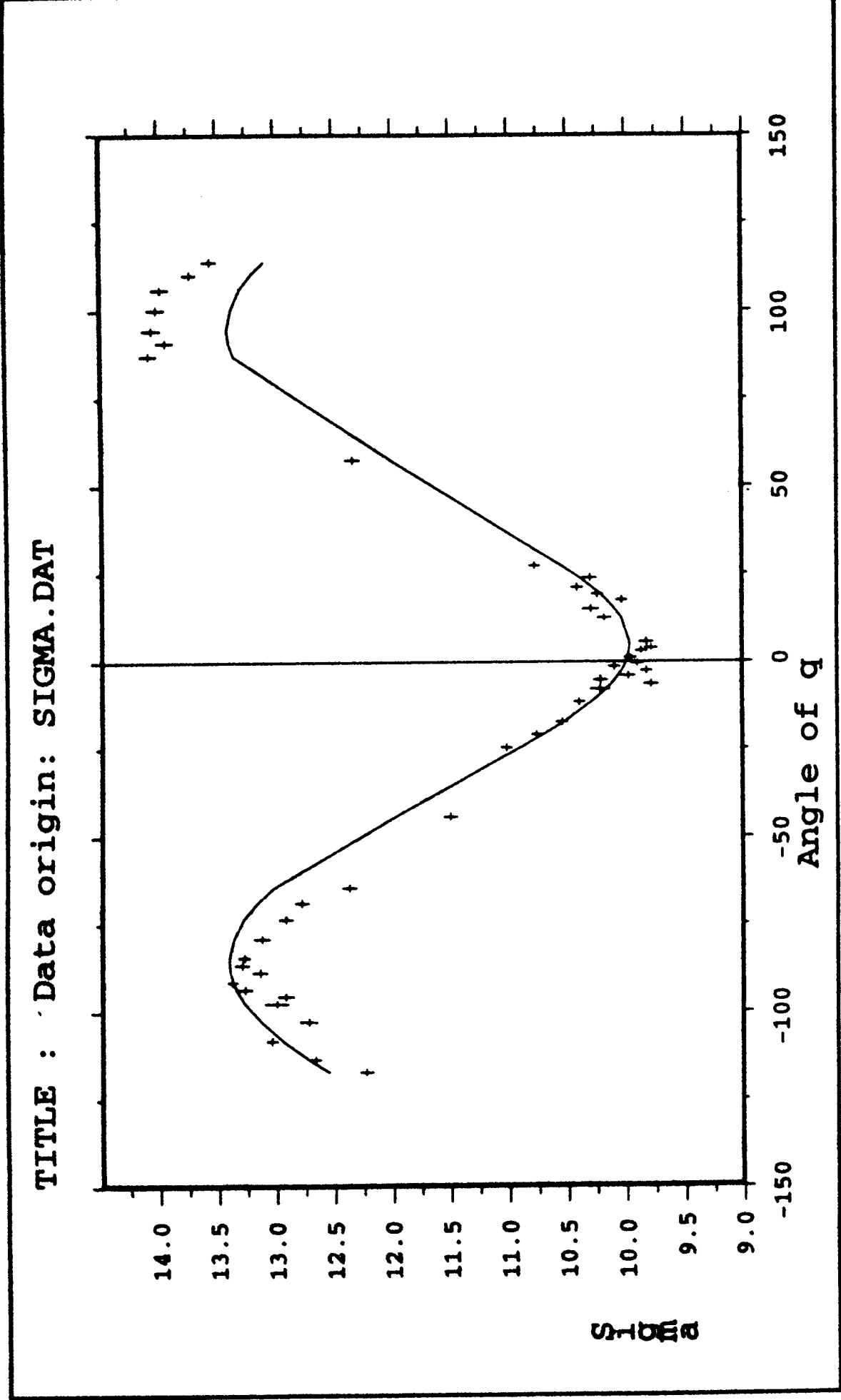


Figure 4. A Genie plot of the widths of the graphite peak as a function of the angle between \vec{q} and the c axis, as described in the text. The solid line is a fit to the data produced by the routine >EFIT.

Reduced Chi-square=17.37

The fit to the data will be stored in workspace W40. The data with fit is shown in figure 4.

Note that the poor value of chi-square (a good fit would give chi-square ~ 1) shows that systematic errors are greater than the statistical errors. The errors given to the parameters should be treated with caution if chi-square is significantly greater than 1, since the errors are purely statistical and do not take account of any systematic errors. The poor chi-square value is also reflected in the fact that the fit does not pass through all the data points. Systematic errors may be due to multiple scattering, faulty detectors or other causes.

Appendix 1. Theory of Time of Flight Fitting

The Impulse Approximation

The theoretical basis of neutron Compton scattering is the impulse approximation (IA), which is exact when the momentum transfer \vec{q} and energy transfer ω are infinite^{1,2} The formal statement of the IA in neutron scattering is³

$$S(\vec{q}, \omega) = \int n(\vec{p}) \delta\left(\omega + \frac{p^2}{2M} - \frac{(\vec{p} + \vec{q})^2}{2M}\right) d\vec{p} \quad (\text{A1.1})$$

where $S(\vec{q}, \omega)$ is the incoherent dynamic structure factor, $n(\vec{p})$ is the nuclear momentum distribution, \vec{p} is the atomic momentum and M is the nuclear mass. The two essential features of the IA are that the neutron interacts with a single nucleus in the sample and that total kinetic energy of the nucleus and neutron is conserved. The latter condition is expressed formally by the δ function in equation A1.1. Using the identity $\delta(ax) = \delta(x)/|a|$, gives

$$S(\vec{q}, \omega) = \frac{M}{q} J(\vec{\hat{q}}, y) \quad (\text{A1.2})$$

where, $\vec{\hat{q}}$ is the unit vector along the direction of \vec{q} ,

$$J(\vec{\hat{q}}, y) = \int n(\vec{p}) \delta(\vec{p} \cdot \vec{\hat{q}} - y) d\vec{p} \quad (\text{A1.3})$$

and

$$y = \frac{M}{q} \left(\omega - \frac{q^2}{2M} \right) \quad (\text{A1.4})$$

$J(\vec{\hat{q}}, y)dy$ is the probability that the nucleus has a momentum component along the direction $\vec{\hat{q}}$ with magnitude between y and $y+dy$. For an isotropic sample there is no dependence of $J(\vec{\hat{q}}, y)$ on the direction of $\vec{\hat{q}}$ and $J(\vec{\hat{q}}, y)dy = J(y)dy$ is the probability that an atom has a momentum component of magnitude between y and $y+dy$ along the an arbitrary direction in space.

The function $J(\vec{\hat{q}}, y)$ is known as the 'Compton profile' and due to its physical significance should be symmetric with a maximum at $y=0$. Equations A1.4 thus implies that $S(\vec{q}, \omega)$ at constant \vec{q} consists of a single peak centred at the 'recoil energy' $\omega_{RM} = q^2/2M$. The corresponding physical interpretation is that a neutron scatters from a stationary atom with an energy transfer ω_{RM} and Doppler broadening due to atomic motion produces a range of energy transfers centred at ω_{RM} .

¹ V. F. Sears Phys. Rev. B 30, 44 (1984)

² J. Mayers Phys. Rev. B 41, 41 (1991)

³ S. W. Lovesey, 'Theory of Neutron Scattering from Condensed Matter', (Oxford University Press, New York, 1987)

Harmonic Systems

If the system under investigation is bound by harmonic forces and the impulse approximation is strictly valid, $J(\vec{q}, y)$ has the Gaussian form

$$J(\vec{q}, y) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(\frac{-y^2}{2\sigma^2}\right) \quad (\text{A1.5})$$

In an isotropic system, the direction of \vec{q} is irrelevant and σ is related to the mean atomic kinetic energy κ via

$$\kappa = \frac{3\sigma^2}{2M} \quad (\text{A1.6})$$

The factor 3 enters because there are three equivalent directions in space for an isotropic system and σ is the *rms* momentum component along one of these (arbitrary) directions.

Final State Effects

One can include a correction for deviations from the impulse approximation, due to the non-infinite momentum transfer \vec{q} and energy transfer ω in the measurement, using the method suggested by Sears¹. He showed that the effects of finite \vec{q} and ω can be accounted for by writing $J(y)$ as,

$$J(y) = J_{IA}(y) + \frac{M\langle\nabla^2 V\rangle}{36\hbar^2 q} \frac{d^3 J_{IA}(y)}{dy^3} + \frac{M^2\langle F^2\rangle}{72\hbar^4 q^2} \frac{d^4 J_{IA}(y)}{dy^4} + \dots \quad (\text{A1.7})$$

where $J_{IA}(y)$ is the impulse approximation result. $\langle\nabla^2 V\rangle$ is the mean value of the Laplacian of the potential energy of the atom and F is the force on the atom. As q becomes sufficiently large, all terms other than $J_{IA}(y)$ can be neglected. In the eVS data analysis routines, the first and second terms on the right are included in the analysis. It is also assumed that the potential is harmonic so that the Compton profile is a Gaussian, of the form given in equation A1.5. In this case $\langle\nabla^2 V\rangle$ can be calculated from the r.m.s. atomic momentum σ . For a 3-D isotropic harmonic oscillator, of frequency ω ,

$$\langle\nabla^2 V\rangle = 3m\omega^2 = 12\hbar^2\sigma^2 / M \quad (\text{A1.8})$$

whereas for a Debye solid,

$$\langle\nabla^2 V\rangle = 12.8 \times \hbar^2\sigma^2 / M \quad (\text{A1.9})$$

Thus FSE can be accounted for in this approximation, without introducing any other parameters than σ .

Fitting in Time of Flight

The energy transfer ω and momentum transfer \vec{q} are calculated from the neutron time of flight t . If E_1 is known, the velocity v_1 of the scattered neutrons can be calculated from $E_1 = mv_1^2/2$ where m is the neutron mass and the velocity v_0 of the incident neutron is determined from a measurement of the neutron time of flight via the equation

$$t = \frac{L_0}{v_0} + \frac{L_1}{v_1} + t_0 \quad (\text{A1.10})$$

where L_0 is the distance from source to sample and L_1 that from sample to detector. t_0 is an electronic time delay constant.

The energy transfer is

$$\omega = m(v_0^2 - v_1^2)/2 \quad (\text{A1.11})$$

and the momentum transfer

$$q = m(v_1^2 + v_0^2 + 2v_0v_1 \cos \theta)^{1/2} \quad (\text{A1.12})$$

where θ is the scattering angle.

The important point is that t uniquely determines ω , \vec{q} and y and conversely, ω , \vec{q} or y uniquely specify t . In particular ω_{RM} defines a unique time of flight t_{RM} which varies with M and which is fixed by the instrument geometry and the atomic mass. Whether the results are analysed in ω , \vec{q} , y_M or t space is a matter of convenience. However in many ways it is most convenient to analyse the data directly in t and this approach is followed in the programs described in this report.

We consider the case where the sample contains a number of different atomic masses. To distinguish between atoms of different mass we add a subscript M . The contribution from atoms of mass M is

$$S_M(\vec{q}, \omega) = \frac{M}{q} J_M(y_M, \vec{q}) \quad (\text{A1.13})$$

The rate at which counts are collected in a time channel of width Δt and centred at time of flight t is⁴

$$C(t)\Delta t = \left\{ I(E_0) \frac{dE_0}{dt} \Delta t \right\} (\eta(E_1) \Delta \Omega \Delta E_1) \sum_M N_M \frac{d^2 \sigma_M}{d\Omega dE_1} \quad (\text{A1.14})$$

The first expression in parentheses is the intensity of incident neutrons with times of flight between t and $t + \Delta t$. The second factor is the product of the detector efficiency η at energy E_1 , the detector solid angle $\Delta \Omega$ and the energy resolution ΔE_1 and is a constant, determined by the instrument geometry and the type of detector. The third factor is the

⁴ C G Windsor 'Pulsed Neutron Scattering', Taylor and Francis (1981)

product of N_M , the number of atoms of mass M in the sample and the double differential scattering cross-section for mass M , summed over all atomic masses present in the sample. The double differential scattering cross-section for scattering from mass M isⁱⁱⁱ

$$\frac{d^2\sigma_M}{d\Omega dE_1} = b_M^2 \frac{v_1}{v_0} S_M(q, \omega) = b_M^2 \frac{v_1}{v_0} \frac{M}{q} J_M(y_M) \quad (\text{A1.15})$$

where b_M is the scattering length of atoms of mass M and equation A1.13 has been used. Taking into account the instrument resolution and the presence of different masses in the sample the final expression for the intensity of scattering at time of flight t is

$$C(t) = \left[\frac{v_1 \eta(E_1) \Delta\Omega \Delta E_1 I(E_0) (dE_0/dt)}{v_0 q} \right] \sum_M N_M b_M^2 M J_M(y_M) \otimes R_M(y_M) \quad (\text{A1.16})$$

where \otimes denotes convolution and $R_M(y_M)$ is the (mass dependent) instrument resolution function in momentum space. The terms in square brackets are sample independent and can be calculated from the calibrated instrument parameters and the time of flight t . Equation A1.16 directly relates the measured time of flight spectra to the atomic momentum distributions of atoms in the sample.

There are two fitting parameters for each atomic mass, A_M and σ_M . The value of σ_M obtained determines the atomic kinetic energy for atoms of mass M , while $A_M = N_M b_M^2$ is determined by the relative scattering intensities of different atomic masses in the sample, ie by the sample composition and neutron scattering cross-sections.

Appendix 2

(a). The TFIT FSE Command File

>TFIT_FSE

ENTER NAME OF OUTPUT FILE. *The output of the program will be stored in a data file with the specified file name. This file can be analysed using the routines \$TPROC and ??.*

ENTER FIRST SPECTRUM. *First spectrum to be processed.*

ENTER LAST SPECTRUM. *Last spectrum to be processed. All consecutive spectra between the first and last will be fitted.*

ENTER ANALYSER ENERGY. *Energy of foil obtained from calibration.*

ENTER ENERGY RESOLUTION. *Foil resolution obtained from calibration.*

ENTER NO OF INSTRUMENT PARAMETER FILE. *Number of IP file.*

ENTER BACK. *If 1 is entered here a linear background is included in the fit. If zero, then no linear background is included. Generally no background is fitted.*

ENTER NUMBER OF PEAKS. *The number of different masses in the sample.*

ENTER ATOMIC MASS 1. *Mass of atom 1 in a.m.u.*

ENTER PRODUCT OF x-SECT AND REL CONC (0 TO FIT). *If zero is entered here, the program will fit the peak amplitude. This parameter can be fixed by entering a non-zero value which is the product of the number of atoms per formula unit and the bound scattering cross-section.*

ENTER PEAK WIDTH (0 TO FIT). *The standard deviation of the (assumed) Gaussian momentum distribution. Again if zero is entered here, the width will be fitted. Otherwise it will be fixed at the value specified.*

ENTER ATOMIC MASS 2. *Mass of atom 2 in a.m.u.*

ENTER PRODUCT OF x-SECT AND REL CONC (0 TO FIT). *As for mass 1*

ENTER PEAK WIDTH (0 TO FIT). *As for mass 1.*

If more than two masses are specified the program will continue to ask for more parameters.

(b) The >DTRANS command

This command converts time of flight spectra to d spacing and is used for the determination of crystal orientation.

>DTRANS

Enter run number 3467

Enter first spectrum 1

Enter last spectrum 32

Enter parameter file number 3455

This sequence of responses will convert spectra 1-32 from run 3467 from time of flight to d-spacing. The instrument lengths and angles required for the conversion are read from the instrument parameter file- in this case 3455.

