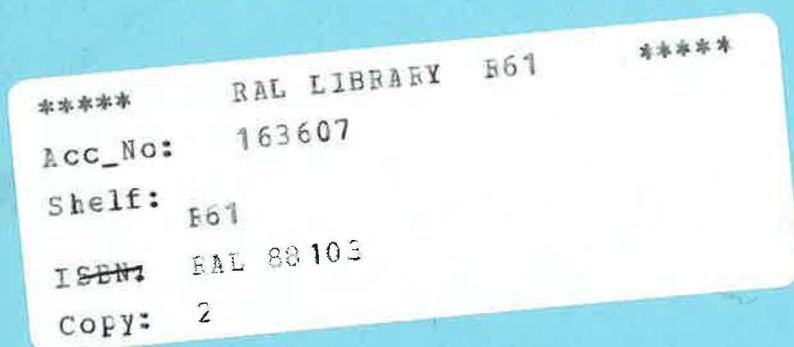Science and Engineering Research Council

Rutherford Appleton Laboratory
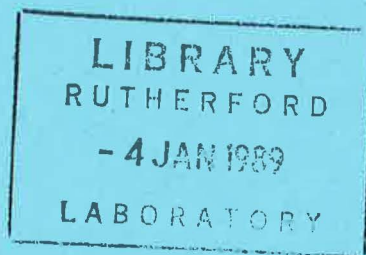
Chilton DIDCOT Oxon OX11 0QX

RAL-88-103

The High Resolution Powder Diffractometer at ISIS - An Introductory Users Guide

W I F David, D E Akporiaye, R M Ibberson and C C Wilson

December 1988

High Resolution
HRPD
Powder Diffractometer
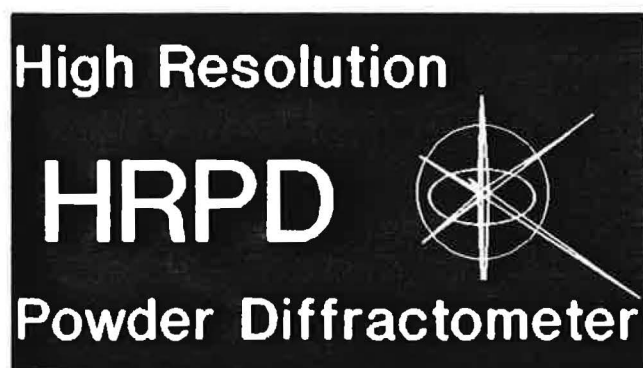
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Version 1.0

May 1988

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APPENDICES

This manual is intended to fulfil the role of an introductory users' guide for HRPD. We hope, in addition to providing a general overview of the machine, that the manual will help users to run the instrument routinely and handle most aspects of data assessment and analysis. The first ISIS powder diffraction workshop is an appropriate occasion to release "Version 1.0". We are aware that we have not been complete in the pages that follow and hope users will take this opportunity to suggest amendments and improvements to the text.

THE HIGH RESOLUTION POWDER DIFFRACTOMETER HRPD AT ISIS

SECTION 1

1 INTRODUCTION

Diffractometers, such as HRPD, at pulsed neutron sources operate in a fundamentally different manner from their conventional reactor-based counterparts. Instead of measuring Bragg reflections by scanning a detector from low to high 2Θ scattering angles, HRPD uses the pulsed white beam nature of ISIS to measure Bragg reflections at fixed scattering angles, monitoring the time of arrival of the neutron after the initial neutron burst produced in the target. Unsurprisingly, this is called the time-of-flight (TOF) method. The relationship between time of flight and d-spacing is linear and can be derived by combining de Broglie's relationship with Bragg's Law as follows :

$$\lambda = h/p_n = h/m_n v_n = 2d\sin\Theta$$

where p_n, m_n and v_n are the momentum, mass and velocity of the neutron respectively, h is Planck's constant with d and $\sin\Theta$ defined according to Bragg's Law. Given a primary flightpath (moderator to sample) of L_1, a secondary flightpath (sample to detector) of L_2 and corresponding times of flight t_1 and t_2 we have :-

$$(h/m_n)\cdot(t_1/L_1 + t_2/L_2) = 2d\sin\Theta$$

Hence with an overall flightpath l and t-o-f t such that:

$$L = L_1 + L_2 \quad \text{and} \quad t = t_1 + t_2$$

this gives:

$$t = 2dL(m_n/h)\sin\theta \qquad \therefore t \propto d$$

Thus for a 10m and 100m instrument, a 1Å d-spacing reflection will be detected in backscattering to have times of flight of ~5000μs and ~50000μs respectively.

1.1 RESOLUTION CONSIDERATIONS

As the neutron production mechanism at a spallation neutron source is rather complicated it is not surprising that the pulse shape is complex. A full account of pulse shape is given in the data analysis section of the manual. A detailed account of instrumental resolution is outwith the scope of this manual however the basic aspects of overall instrumental resolution (for a TOF powder diffractometer) may be obtained in a simple manner.

Consider neutrons of a particular wavelength, λ. They may be "born" at either the front or the back of a moderator, a distance uncertainty , ΔL, typically of the order of 5cm. Because of the slab shape of the moderator this gives an associated full-width-at-half-maximum (FWHM) fractional flight-path uncertainty, $\Delta L/L$, of 0.034/L(metres) which because of the linear relationship between L, t and d gives:

$$(\Delta L/L) = (\Delta t/t) = (\Delta d/d)(\text{moderator}) = 0.034/L(\text{metres})$$

Thus, neglecting other resolution terms (a good approximation in backscattering), it follows that resolution improves linearly with distance.

Other resolution terms arising from geometrical uncertainties associated with sample (S) and detector (D) size may be gathered together in variance form as

$$\sigma^2 = (\Delta l/L)^2 + \{(\Delta\theta_1)^2 + (\Delta\theta_2)^2\}\cot^2\theta$$

where

$(\Delta l)^2$ = sum of squares of distances travelled in sample and detector

L = overall flight path

2θ = scattering angle

$\Delta(2\theta_1)$ = uncertainty in incident angle from extended sample and moderator/guide/pre-collimation

and $\Delta(2\theta_2)$ = uncertainty in scattering angle from extended sample and detector

An empirical measure of TOF powder diffractometer resolution may be obtained from the full-width at half-maximum expression

$$(\Delta d/d)_{FWHM} = (0.034/L) + 0.0029\sqrt{\left[LENSQ + (BEFSQ+AFTSQ)*cot^2\theta \right]}$$

where

$$LENSQ = 4(\eta_i^2 S_i^2 + \eta_o^2 S_o^2 + \eta_D^2 D_D^2)/L$$

$$AFTSQ = (\eta_o^2 S_o^2 + \eta_W^2 D_W^2)/L_2$$

$$BEFSQ = \begin{cases} (\eta_i^2 S_i^2 + 4M^2/3)/L_1 & -\text{ beam tube} \\[2ex] (0.4\lambda)^2 & -\text{ Ni guide} \\[2ex] (0.034\Delta\phi)^2 & -\text{ Soller collimation} \end{cases}$$

where the shape factors, η, equal 1 for cylindrical and 4/3 for slab geometry: M, S and D are moderator, sample and detector widths respectively (in cm.) – L_1, L_2 and L (in m.) are respectively primary, secondary and overall flight paths. The subscript notation is as follows:

i ≡ sample shape "seen" by incident beam

o ≡ sample shape "seen" by outgoing beam

D ≡ depth of detector

W ≡ width of detector

λ is the neutron wavelength (Å) and $\Delta\phi$ is the Soller collimation angle (in minutes).

2 INSTRUMENT SPECIFICATION

The instrument specification reflects the paramount aim of producing an instrument with resolution of $\Delta d/d \sim 4 \times 10^{-4}$ using a pulsed neutron source, see Johnson and David (1985) and David, Harrison and Johnson (1986). A schematic layout of HRPD is shown in figure 1.

2.1 MODERATOR

The correct moderator design is crucial for the diffractometer since the ultimate limit to the resolution is decided by the pulse width $\Delta t(\lambda)$ and neutron flight-time $t(\lambda)$. The HRPD 95K gadolinium poisoned liquid methane moderator gives the required "tight" neutron pulse time structure over a wide range of wavelengths (Taylor 1982). Full details of predicted moderator performance are given in Taylor (1984).

The resultant flux distribution is shown in figure 2, it can be seen the maximum flux occurs with neutrons with a wavelength of ~2Å and beyond ~5Å the flux is considerably reduced.

2.2 GUIDE TUBE

Reduction of the ($\Delta L/L$) term necessitates the long (~100m) primary flightpath of HRPD and so to achieve acceptable intensities a guide is used. It can be shown (Carlile, Johnson and Williams 1979) that incorporation of a guide creates an effective flightpath of $\sim 29/\lambda$ m thus the increase in neutron flux is considerable, as illustrated in figure 2. The guide incorporates a curved section in order to eliminate the adverse effects of the short time γ and fast neutron pulse, there being no direct line of sight from moderator to the sample and detectors.

The guide itself consists of a nickel plated glass tube with cross-section 8cm x 2.5cm. The guide tube has a radius of curvature of 18km extending from 6m to 60m from the moderator.The following 60m to 96m section is straight to facilitate the smoothing of beam intensity inhomogeneities in the guide. The parameters used represent the optimised configuration for a 50Hz source; details of the simulation techniques are given in Carlile, Johnson and Williams (1979).

The radius of curvature is sufficiently shallow to transmit sub-angstrom neutrons however the guide "cut-off" is such that no neutrons are transmitted with $\lambda \leq 0.5$Å.

HRPD Instrument Layout

95K liquid methane moderator

Shutter

6m Chopper

9m Chopper

Curved Guide
(18km radius)

HRPD

R69

Figure 1

TITLE : HRPD Flux at the 1m sample position
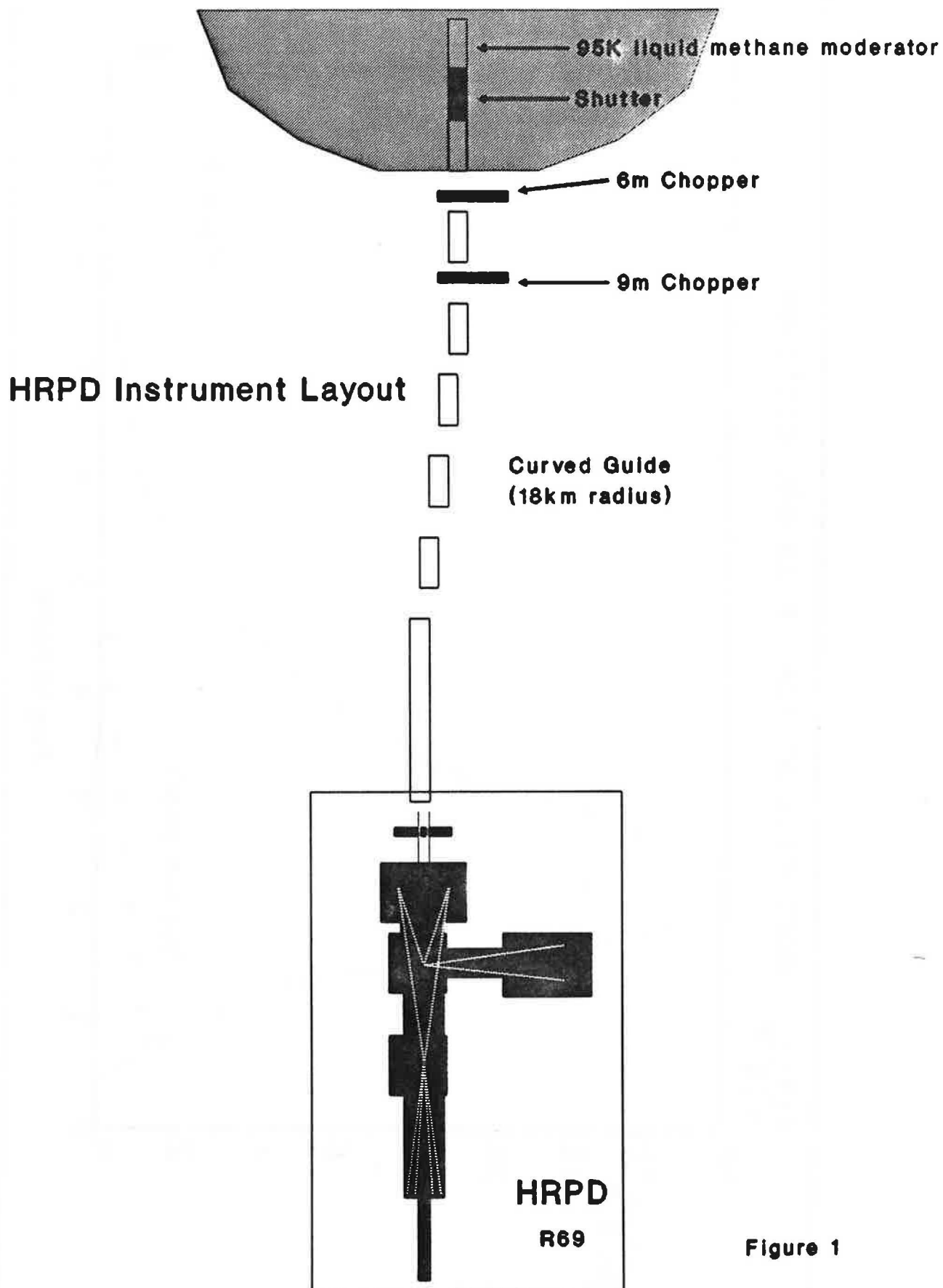
Figure 2
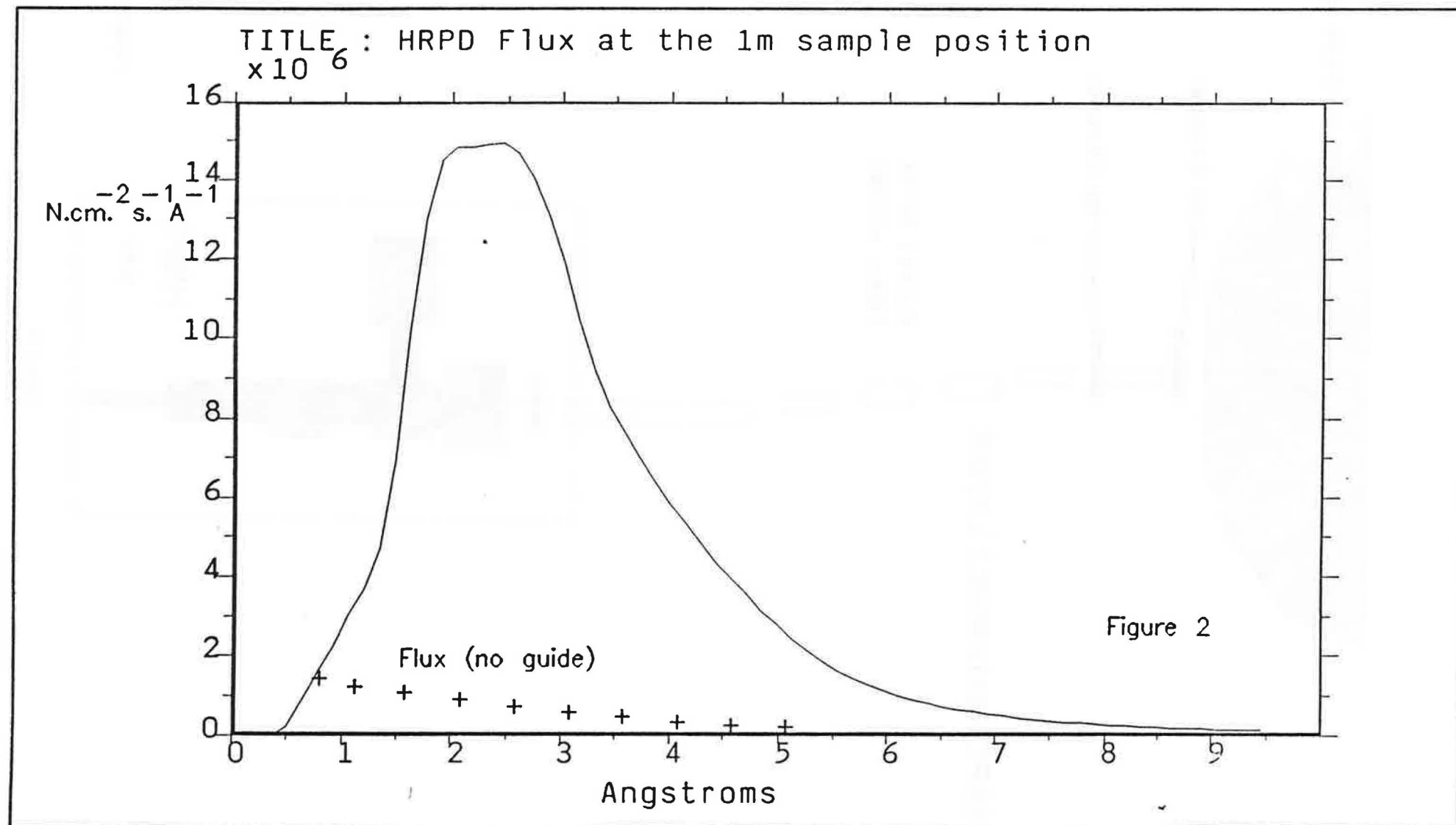
2.3 CHOPPERS

The long overall flightpath of HRPD introduces the problem of "frame overlap" from successive neutron pulses. This is eliminated by the use of two beam choppers situated at 6.135m and 9.2m from the moderator. The first disk chopper rotates at ISIS frequency (~50Hz) and acts as the wavelength "selector" whereas the second chopper rotates at (50/n)Hz preventing frame overlap. This is illustrated in figure 3. Neutron pulses occur at A, B, O and C with OO'-OO" representing the transmitted rays. The 9m chopper (C2) stops rays AA'-AA", BB'-BB" and CC'-CC" in addition to the first harmonics form A and B which are shown dotted.

In practise this allows neutron wavelength "windows" of widths 0.4Å, 0.8Å or 2.0Å to be selected out of the overall incident flux spectrum. The actual wavelength range of incident neutrons within each window depends on the phasing of the choppers relative to the initial neutron pulse.

2.4 SAMPLE TANK

A schematic diagram of HRPD is given in figure 4. The incoming beam is collimated by motorised jaws operating in the horizontal and vertical planes. Two sample positions are available, sited at 1m and 2m from the backscattering detector. Maximum resolution is obtained using the 2m position. However, as a slight degradation in resolution is unnoticed with the majority of samples, the 1m position is to be favoured since this gives a factor four increase in intensity.

The external fast neutron background is minimised by the incorporation large quantities of borated wax in the sample tank design. In addition the entire tank is lined with boron carbide resin tiles to prevent multiple scattering of thermal neutrons within the tank.

The tank is evacuated to a nominal 10^{-1} torr but the capability to reach 10^{-6} torr and below exists, for use in conjunction with sample environment equipment.

Chopper ray diagram

Figure 3

Guide tube

Jaws

Monitor

Backscattering
Detector

1m Sample
Position

90 degree
Detector

2m Sample
Position

Low angle
Detector

Monitor
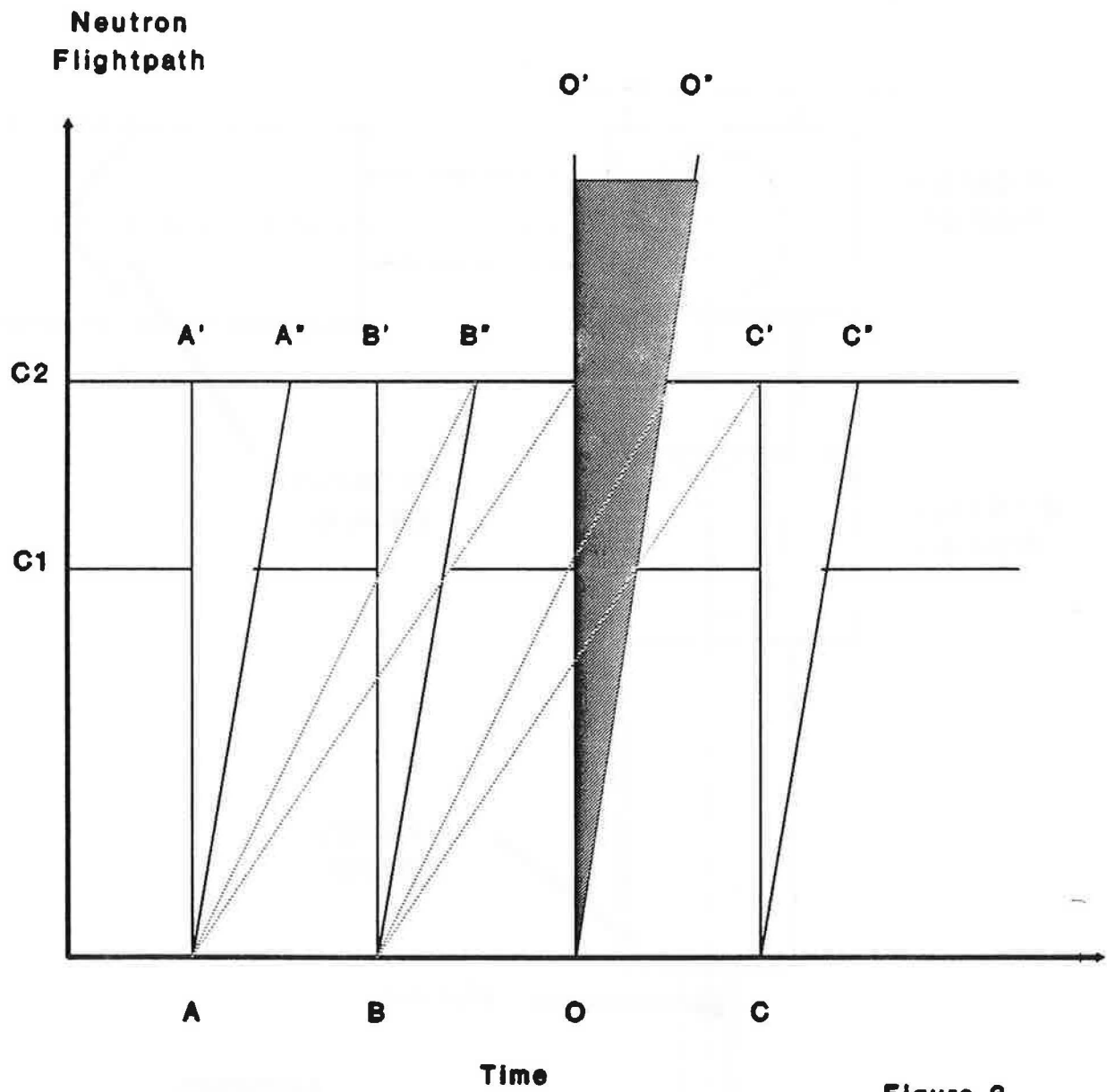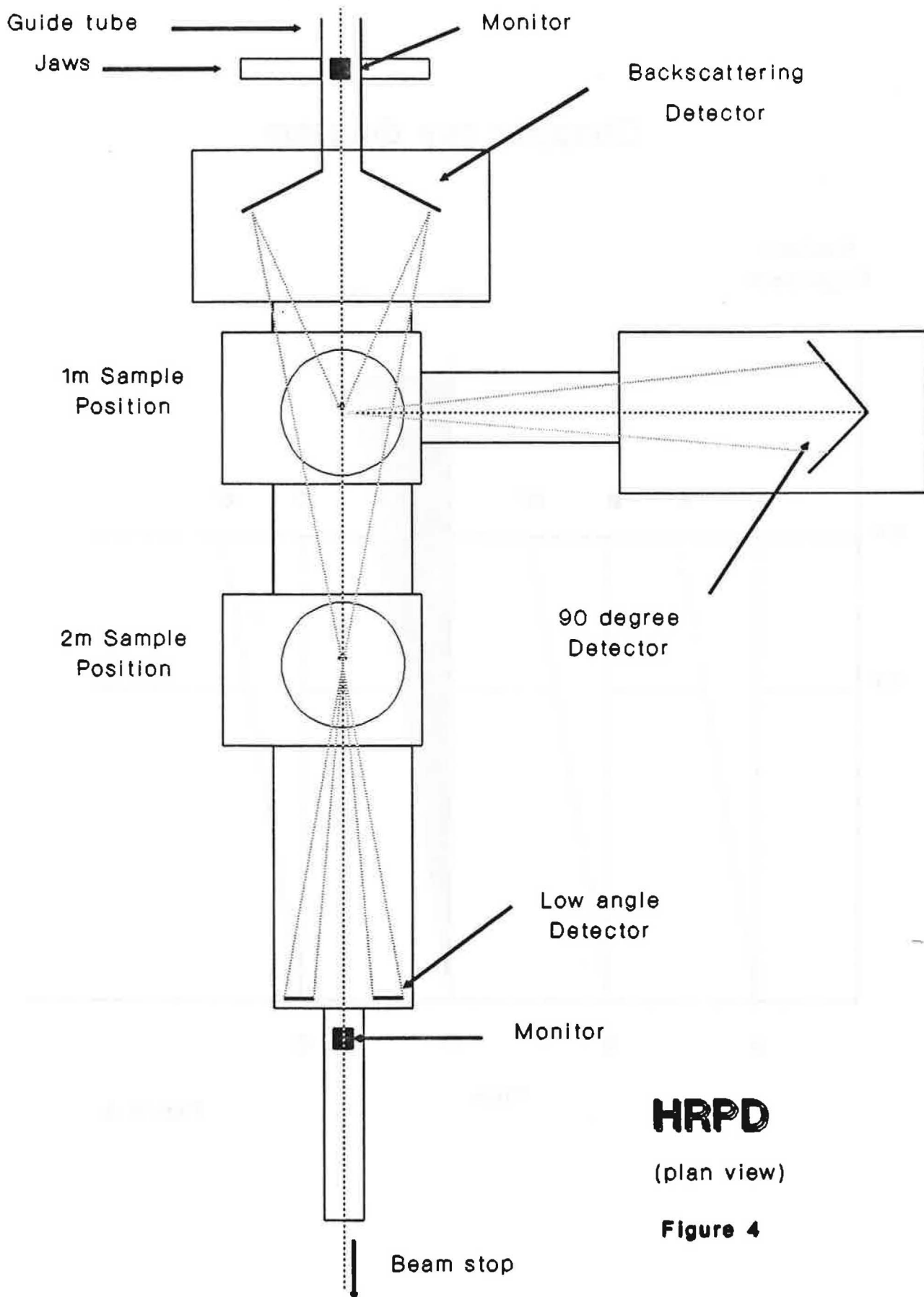
HRPD

(plan view)

Figure 4

Beam stop

page 14

2.5 DETECTORS

Three main banks at backscattering, 90° and low angle comprise the HRPD detector configuration. At present all utilise cerium-activated Li^6 glass scintillator.

The scintillator background is designed to be below 1 count per minute per cm^2. In a typical run this gives rise to a flat background of $\sim$ 10cts/µs for the whole backscattering detector. Electronic background is predicted to be at least two orders of magnitude less than the above values and so is considered to be negligible.

The backscattering detector consists of eight octants, so constructed to form 20 concentric detector rings. At high angles the resolution is best as $\Delta\theta\cot\theta$ is reduced, in addition the concentric detector geometry matches that of the Debeye-Scherrer cones thus eliminating geometrical contributions to the profile line shape. At present only six octants are installed. Hence the detector is comprised of 120 elements (ie. 6x20 individual ring segments) Using a fibre-optic encoding system the elements may be linked as desired to produce a position sensitive detector.

The low angle detector consists of 12 elements forming a ring . It is usually the case that both the backscattering and low angle detector elements are linked to form discrete annular rings so that twenty spectra are collected at backscattering and one spectrum at low angle.

The 90° detector bank in contrast will utilise recently developed ZnS detectors which give an improved signal-to-background ratio and show no gamma sensitivity. At present the 90° detector bank is in the commissioning stage and a Li-glass scintillator module is installed. The module provides one hundred optically distinct 150x3mm detector elements.

The incident and transmitted beam intensity is monitored by two

page 15

Davidson monitors (Davidson 1985) situated at 93.46m and 97.05m respectively from the moderator.

Detector details are summarised in table (1).

Table 1 Detector Parameters

	Backscattering	90° Bank	Low angle
Dimensions	$3 \leq r_1 \leq 4.5$cm $35.5 \leq r_{20} \leq 37$cm	15 x 30cm	r = 45.0cm
Elements	120 / 20 rings	100	12 / 1 ring
2θ (@ 1m)	$176° \leq 2\theta \leq 160°$	$87° \leq 2\theta \leq 93°$	5°
2θ (@ 2m)	$178° \leq 2\theta \leq 170°$	n.a.	7°
Ω (@ 1m)	0.37 ster	0.3 ster	0.001 ster
Ω (@ 2m)	0.1 ster	n.a.	0.002 ster
$\Delta d/d$(@1m)	$\sim 5 \times 10^{-3}$	$\sim 1 \times 10^{-3}$	$\sim 3 \times 10^{-2}$
$\Delta d/d$(@2m)	$\sim 4 \times 10^{-4}$	n.a.	$\sim 3 \times 10^{-2}$

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[1] Johnson M W and David W I F (1985) HRPD : The High Resolution
     Powder Diffractometer at the SNS. Rutherford Appleton Laboratory
     Report 85-112.

[2] David W I F ,Harrison W T A and Johnson M W (1986) Initial Results
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     Rutherford Appleton Laboratory Report 86-068.

[3] Taylor A D (1982) Moderated neutron pulse shapes. Argonne National
     Laboratory Report 82-80.

[4] Taylor A D (1984) Moderator performance predictions. Rutherford
     Appleton Laboratory Report 84-120.

[5] Carlile C J ,Johnson M W ,Williams W G (1979) Neutron Guides on
     Pulsed Sources. Rutherford Appleton Report 79-084.

[6] Davidson P L (1985) Thermal neutron beamline monitor. Rutherford
     Appleton Report 85-032.

THE EXPERIMENTAL RUNNING OF HRPD

SECTION 2

1 ADMINISTRATION REQUIREMENTS

HRPD is located in R69, outside and south of R55, the main experimental Hall (see map Appendix 1). On arrival however users are requested first to fulfil the following requirements before commencing their experiment.

- Register with the University Liasion Secretariat, UG floor R3. This is of particular importance if accommodation has been booked and also with regard to the claiming of expenses.

- Fill in sample record sheet, see Brian Boland room 2.31 R3. If a record sheet has already been completed and returned prior to the experiment it will be available in R69.

- Collect temporary radiation film badges from the Main Control Room in R55. Both R69 and R55 are restricted areas therefore Health and Safety requirements necessitate the wearing of film badges.

All users are required to complete Experimental Reports. An informal A4 report should be completed at the time of the experiment and the A3 report within three months of the experiment. Report forms are available from the University Liasion Secretariat or Instrument Scientists.

2 SAMPLE LOADING

Since an increase in sample volume will, in general, decrease the required counting time, as large a sample can as possible should be used. The exceptions to this are with hydrogenous samples, where sample can area should be increased at the expense of thickness, or with strong neutron absorbing samples.

The standard HRPD can is of a slab geometry with volumes of $1cm^3$ up to $6cm^3$. The can comprises of an aluminium body with thin vanadium windows attached by aluminium window frames. **These cans are not sealed.**

A cylindrical "Harwell can" of vanadium construction may also be used on HRPD. Depending on sample environment the Harwell can may be appropriately sealed unlike the slab can. Both cans may be used regardless of sample environment but in order to collect data at 90° a Harwell can should be used.

2.1 ROOM TEMPERATURE EXPERIMENTS

The aluminium of the filled can is shielded using either a Li-glass or a Gd-foil mask. The can and mask assembly is attached to the centre stick with an M4 fixing bolt. The incoming beam is 310mm from the lower flange on the lid, so the flange-can window distance should be adjusted to this, as shown schematically in figure (5) .
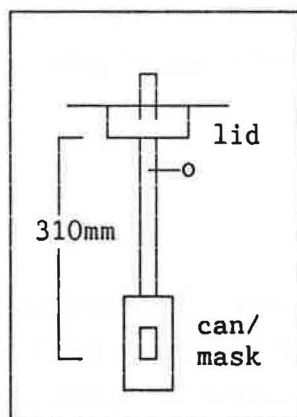
Figure 5

2.2 SAMPLE TANK EVACUATION

In order to reduce air-scattering and usually with all sample environments, the sample tank is evacuated before the commencement of data collection.

Valves are located at the far side of the raised platform alongside the 90° detector tank. The "roughing pump" situated inside the guide tunnel **runs continuously** so should not be touched. To vac down, fully close the valve labelled "back-to-air" then slowly open the valve above it connected to the pump. After some 30s this valve may be opened fully. To let the tank up to air the latter valve is first closed before slowly opening the "back-to-air" valve. Letting up to air takes some twenty minutes.

The "turbo pump" situated alongside the sample tank should remain switched off unless pressures of $<10^{-3}$ torr are required, normally only when using a closed cycle refrigerator (CCR).

2.3 OPENING THE BEAM SHUTTER

An interlock mechanism exists preventing the shutter from being opened while the door to the instrument compound is open. The door must first be locked and the key located in the green shutter marshalling box

alongside, before the "open" and "close" buttons will function. Opening and closing operations take approximately one minute.

3 CHOPPER SETTINGS AND CONTROL

Two disk choppers are situated at 6m and 9m from the moderator. Direct access to them is not required, only occasionaly to their Cortina power units, which are located by the LAD cabin in the main hall (R55), see map (Appendix 1). All chopper settings may entered using the CAMAC system however values can also be entered manually on the crates in rack 4, under the raised instrument platform in R69.

3.1 CHOPPER ROTATION SPEED

The "width" of the incident neutron pulse is determined by the chopper speeds, as shown below in table 2 :

Chopper speed (6m)	(9m)	Pulse width		Relative beam intensity
50Hz	10Hz	100ms	(2.0Å)	0.2
50Hz	16.6Hz	60ms	(1.2Å)	0.3
50Hz	25Hz	40ms	(0.8Å)	0.5
50Hz	50Hz	20ms	(0.4Å)	1.0

Table 2

The instrument is normally run with the 100ms pulse width to give the widest wavelength range of spectrum. A specific part of the spectrum may be looked at using the other settings thus gaining beam intensity at the expense of spectrum range.

Using CAMAC rotation speeds can be reset as shown below :

```
$ CSPEED6 50

$ CSPEED9 10
```

Rotation speeds cannot be reset while the choppers are running so the above commands involves stopping and restarting both choppers. Red error LED's on the rack 4 will go out once both choppers are at speed, this may take up to 10 minutes.

Stop and start buttons on the rack allows manual resetting. When stationary, shown by the rotor speed indicator on the rack, select the desired speed using the dial on module 1 and press the "enter data" button.

3.2 CHOPPER PHASING

The chopper phasing determines the actual wavelength range of the neutrons and is selected using an "offset" value. The offset values must be correctly set to give the required minimum t-o-f value of the neutron pulse. A table of offset values is given in Appendix 2.

Using CAMAC both chopper offsets are set by entering the required minimum time-of-flight as shown below :

```
$ CPHASE 30

    6m chopper at 50Hz  offset=1177ms
    9m chopper at 10Hz  offset=2523ms
    This gives a spectrum of 30000ms-130000ms (0.6-2.6Å).
```

Offset values may be manually entered via the module 3 thumb-wheels and by pressing the "enter data" buttons. Once in phase the red error LED's in module 6 will go out. In both cases a run must not be started until then, (see figure 6) .

```
+--------+---------------+-------+-----+-----------------------+
|        | 3             | 6     |     |                       |
|        |  +-+-+-+-+-+   |       |     |                       |
|        |  |0|0|0|0|0|   | o<-error     6m chopper control    |
|        |  +-+-+-+-+-+   |   light |   |                       |
| enter |data->o         |       |     |                       |
|  button|              |       |     |                       |
+--------+---------------+-------+-----+-----------------------+
|        | 3             | 6     |     |                       |
|        |  +-+-+-+-+-+   |       |     |                       |
|        |  |0|0|0|0|0|   | o     |     9m chopper control     |
|        |  +-+-+-+-+-+   |       |     |                       |
|        |       o       |       |     |                       |
+--------+---------------+-------+-----+-----------------------+
```
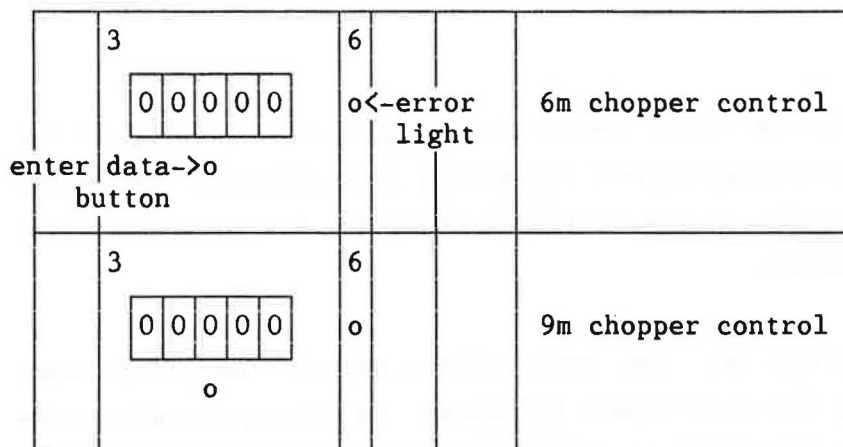
Fig 6   Modules 3 & 6, Rack 4

4 DATA ACQUISITION AND INSTRUMENT CONTROL

Data acquisition on HRPD is carried out using a microVax(II) computer, also known as a FEM (Front End Monitor). While a run is in progress data is temporarily stored in the Data Acquisition Electronics (DAE). At the end of each run data is **automatically** written to a file of the form **HRP**"run number".**RAW** and stored on the microVax(II) aswell as being transferred to the main Hub computer, a Vax 8650. All raw data files are then archived, this involves copying to magnetic tape or optical disk for permanent storage.

HRPD is controlled using the microVax, instrument commands are issued from an operator terminal on which the instrument "dashboard" is normally displayed.

4.1 THE DASHBOARD

The instrument dashboard shows details of the current run and displays

the DAE mode (see 4.2). The commands **STAT ON** and **STAT OFF** turn the dashboard display on and off,a typical dashboard display is shown below (figure 7):

HRPD IS **RUNNING** RUN 1350

Tue 12-Apr-1988 12:17:12		TEMP LOG 146.5
User: Team HRPD Tel: 5179/5871		---raw---> 13.9
Title: YBa2Cu307-x (variable temp)		TEMP1 LOG 140.1
Current run time 0 01:10:32	MONITOR	---raw---> 12.8
Current/Total uA 15.2/26.8	Spectrum 23	CPHS6 TRUE 1177
Good/Raw frames 7707/7710	From(mms) 50000.0	CPHS9 TRUE 2523
DAE memory used.Bytes349423	To (mms) 55000.0	
25 Spectra 14664 Channels	Counts = 1345738	

Figure 7

The information shown is essentially self-explanatory. As data is collected both frame count figures and the monitor count value should all be increasing.

A frame is the period between ISIS neutron pulses. On HRPD the beginning of each frame is defined by **two** synchronisation (synch) pulses, one from the synchrotron and one from the 6m chopper. The prerequisite of a good frame, during which data is added to the DAE, is the trigger from **both** these pulses. If the frame is not good a veto suspends DAE data collection. On HRPD a "raw frame" is defined solely by the chopper synch pulse, so that an incrementing raw frame count serves only to indicate that the chopper is running.

The monitor count normally refers to the downstream monitor situated

behind the sample. The figure shown is the integrated counts between the limits shown over the monitor spectrum shown.

4.2 THE DAE

The DAE (Data Acquisition Electronics) governs data collection for each individual run. It correlates parameters from a number of files but it should be necessary only to edit the CRPT (see 9.3) and possibly to select the appropriate SPECTRA.DAT (see 9.2) file before commencing a run.

There are four possible modes of the DAE :

    SETUP   - No data recording taking place, parameters may be changed prior to a run.

    RUNNING - Data recording in progress.

    PAUSED   - Data recording temporarily suspended due to an interactive user issued command.

    WAITING   - Data recording temporarily suspended due to an out of range parameter in a CAMAC sample environment block.

DAE mode and the current run status are displayed on the dashboard.

4.3 DEFINING A SPECTRA.DAT

The SPECTRA.DAT file can be considered as determining the configuration of the detectors. One of three standard files are normally used.

4.3.1 SPECTRA.DAT_25

This is most commonly used giving the standard configuration for the

back-scattering detector. Spectra 1-20 constitute the annular rings of the detector which can then be summed. Spectrum 21 is the annular ring of the low angle bank and spectra 22 and 23 the upstream and downstream monitors respectively.

4.3.2 SPECTRA.DAT_90DEG

This should be used in order to utilise the 90° bank. The numbering of the spectra is as above with spectra 26-100 containing 90° data.

4.3.3 SPECTRA.DAT_125

This file leaves all detector elements discrete in backscattering - thus there is no linkage to form rings. Such a configuration would be suitable for textural studies. Spectra 1-120 are in backscattering, spectra 121, 122 and 123 are the low angle bank and monitors as before.

4.4 INSTRUMENT COMMANDS

Data collection is controlled using five basic instrument commands which must be issued from the operator terminal.

BEGIN – sets DAE memory to zero
        – sets parameters in DAE to those specified by CRPT
        – sets DAE to acquire data
        – sets DAE mode to RUNNING

PAUSE – suspends data collection by DAE
        – sets DAE mode to PAUSED

RESUME – resumes data collection by DAE
        – sets DAE mode to RUNNING

END   – stops data collection
        – copies DAE memory and CRPT to HRP"Run no.".RAW
        – dashboard run number is incremented
        – sets DAE mode to SETUP

ABORT – stops data collection
        – <u>no data is stored</u>
        – sets DAE mode to SETUP

The relationship between DAE modes and instrument commands is shown below in figure 8. Instrument commands are shown in **BOLD**.
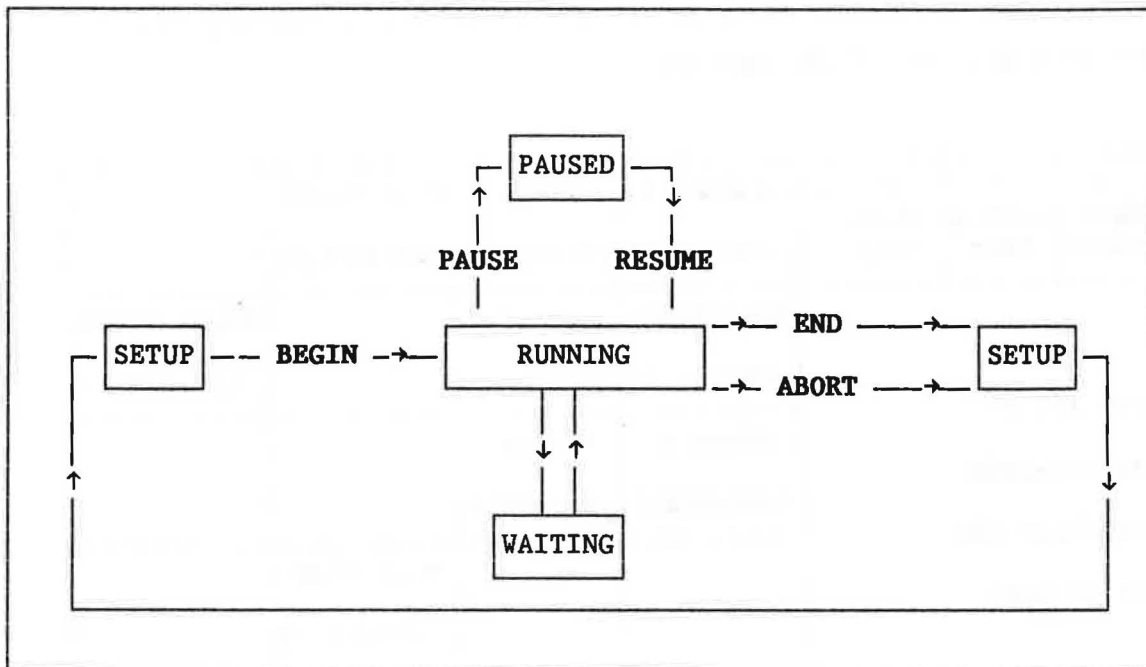
Figure 8

4.5 THE CRPT

The CRPT (current run parameter table) file acts as an intermediary data storage file between the DAE and the final stored raw data file. In addition it contains the settings of various run parameters

It is normally necessary to edit the run parameter section of the CRPT prior to **every** run. This section is accessed by the command **CHANGE** when the DAE is in SETUP mode. **CHANGE** presents the user with the appropriate pages of the current CRPT, values are altered using full screen editing techniques (DEFT).

Pages from a typical CRPT is shown below with explanatory notes. The cursor keys (↑ ↓) allow movement between the various fields, when the field prompts with "toggle data type" the "." key on the right hand key-pad should be used. To exit and overwrite the CRPT with the new values hit **GOLD E** or to quit, leaving the CRPT as it was, hit **GOLD Q**.

The DEFT key pad layout is shown below in figure 9 . It corresponds to the right hand key-pad of the terminal

↑ Back a Field	↓ Next Field	← Back a Char	→ Next Char

Key-pad layout
|
for the commands

to manipulate the

screen in DEFT

(**Toggle** variables can only be changed with the toggle key)

Figure 9

End/Quit (GOLD) F1	Help (HELP)F2	Next Field (FINDNXT)F3	
Next Page (PAGE) 7			Clear Field (DLWORD) −
Advance (ADVANCE)4	Backup (BACKUP)5		
		Next Char (CHAR) 3	
		Toggle (SELECT) .	

EXAMPLE - The information in each field is shown here in **bold**. In the actual CRPT each field is defined in reverse-video

```
page  1
HRPD CONTROL PROGRAM :  User Information              page 1 of 5

RUN TITLE -----SHORT---> ================= LONG ====================>

YBa2Cu307-x RT


                PROPOSAL NUMBER : RB999

   USER NAME: Team HRPD              INSTITUTION:R.A.L.


   Telephone Nos. for contact during experiment
            Day WIFD 5179 / RMI 5871
```

Page 1 : All fields are self-explanatory.

```
page  2
HRPD CONTROL PROGRAM : Time Channel Boundaries          page 2 of 5

Method of deriving time channel information:>

 Use the parameters below to construct a SINGLE spectrum

  FROM(mms)       TO(mms)       steps        in mode

   12000          16000          100           dT=C

   16000          112000         0.0001        dT/T=C

                                               dT/T=C

                                               dT/T=C

                                               dT/T=C

  DISPLAY MONITOR: Spectrum 23   Region (mms) 50000 to 55000
```

Page 2 : The range of the spectrum should obviously correspond to that
which the choppers have been set to. The method of deriving the time
channel boudaries is usually to fill in the fields shown on the page. If
there is insufficient space, for example with a very complex spectrum
construction, a seperate file, TCB.DAT which defines the boundaries, is
set up. By entering the file name on the first line, the time channel
boundaries are set by reading the file only.

Steps of 0.0001 in mode dT/T=C give time channel boundaries of
instrument resolution. Many samples do not warrant this treatment so a
value of 0.0002 or greater could equally well be used, giving the
advantages of a reduced memory requirement and increased speed of data
manipulation. Mode dT=C should be used over areas where detail is not
required in order to reduce the memory requirement.

The   Status Display Monitor   corresponds with the   monitor count
information shown on the dashboard. Spectrum 23 corresponds to the
downstream monitor and is used in most configurations. The displayed
number of counts on the dashboard is the integral between the two limits
set in the CRPT. This region is generally placed somewhere in the middle

of the spectrum.

```
┌────────────────────────────────────────────────────────────────────┐
│ page 3                                                             │
│ HRPD CONTROL PROGRAM : Sample Environment              page 3 of 5 │
│                                                                    │
│ Sample type             1: Sample                                  │
│ Sample height (mm)       20                                        │
│ Sample width (mm)        15                                        │
│ Sample thickness (mm)    10                                        │
│                                                                    │
│ Sample can type    1:HRPD slab      Sample geometry   1:Flat plate │
│                                                                    │
│ Beam aperture (horizontal)  20 mm        (vertical)   25 mm        │
│                                                                    │
│ Scattering position          1m               Vacuum  ON           │
│                                                                    │
│ *********************************************************************│
│              THE REMAINING PAGES SHOULD NOT BE ALTERED             │
│                                                                    │
│       Type GOLD ('F1') E to exit, Q to quit or C to continue       │
│                                                                    │
└────────────────────────────────────────────────────────────────────┘
```

Page 3 : All fields are self-explanatory. As indicated the remaining pages under normal circumstances should remain unchanged.

```
page  4
HRPD CONTROL PROGRAM  :  Instrument settings              page 4 of 5


SNS frequency = 50/2**k where 2**k = 1

DAE synch source    ISIS

Moderator type        1:(B)FRONT CH4 90K eq.pd= 20mm

Main shutter          OPEN

Thermal shutter       ABSENT

End run at                        Update every
```

Page 4 : Values will remain constant except under special circumstances.

```
page 5
HRPD CONTROL PROGRAM : Data Acquisition Electronics       page 5 of 5


Word length to be used in DAE bulk store       32   bits

 (ie. maximum count before overflows = 4 billion   )


Collect data in synch with chopper only?  YES

How many periods do you wish to use  ?  1
```

Page 5 : The fields should not be changed without consulting instrument

scientists.

5 CAMAC - THE SAMPLE ENVIRONMENT CONTROL SYSTEM

The CAMAC (Computer Aided Measurement and Control) system provides the means of maintaining a particular environment for the sample during data collection. Thus from the CAMAC hardware interface linking the Eurotherm temperature controller it is possible to control data collection, via the operator terminal, with respect to sample temperature. Hardware for sample orientation is also available.

CAMAC data is displayed in the right-hand block of the dashboard. A value of resistance from the Eurotherm is displayed aswell as the conversion to K or °C for each temperature reading.

5.1 CAMAC COMMANDS

All commands to change parameters are typed at the $ prompt from the operator terminal. Most are of the form **CSET** name/qualifier or **CSHOW** name/qualifier: where "name" is usually a variable to be altered such as TEMP. A basic guide to CAMAC temperature control is given below, readers are referred to the Punch User Guide for full details.

5.1.1 Initialisation

It may be necessary to intitialise the temperature controller before any of the following commands will work. The format of the command is:

$ CSET TEMP/INI

5.1.2 Setting

To change the set-point within the Eurotherm, that is the temperature value the control device will attempt to reach:

```
$ CSET TEMP value
```

or

```
$ CSET TEMP/VALUE=value
```

Where value is the desired temperature.

5.1.3 Limits

These commands define the cut off points for data collection as the "block" TEMP is a run control parameter. To define symmetric limits about the current desired value the format is:

```
$ CSET TEMP/RANGE=value desired_value
```

This defines temperature limits of desired_value$\pm$(value/2).

It is also possible to define non-symmetric limits using the qualifiers HILIMIT and LOLIMIT.

5.1.4 Run Control

If the block is a run control parameter, should the parameter go out of bounds of the defined limits then data collection is suspended, that is the DAE goes to WAITING mode until the parameter is in range. The command is:

```
$ CSET TEMP/CONTROL
```

To stop it being a run control parameter the command is:

```
$ CSET TEMP/NOCONTROL
```

5.1.5 Display

This command will cause the current value of the control block to be

displayed on the dashboard:

    $ CSET TEMP/DISPLAY

To stop the display:

    $ CSET TEMP/NODISPLAY

5.1.6 Logging

The command causes the current value of a particular temperature sensor
to be returned from the hardware source once every n seconds:

    $ CSET TEMP/LOG=n

The value n is optional and the default setting of n=10 is recommended.
It is conventional on HRPD to log the sample temperature from the sensor
with address 0 on the Eurotherm (the right-hand controller). To log the
temperature of any other sensor the command is:

    $ CSET TEMPn/LOG

Where n is the address of the sensor. 1 is normally the address of the
left hand controller which will show cryostat or furnace temperature as
oppose to actual sample temperature.

5.1.7 Closing the logfile

The option to close the current logging file and implicitly open a new
one is:

    $ CSET CAMAC/CLOSE=filename.ext

The filename is optional and normally is omitted, the default usually
being appropriate.

5.1.8 Displaying the logfile

Having closed a logfile it may be displayed by running a GENIE command file. Once in GENIE the command is:

    >>
    >> **TEMP**

or

    >>
    >> **TEMP1**

The program will prompt for start and finish times, hit **<ret>** for the complete logfile, and for "SE block" which in this case is **TEMP**. The logfile plots are read into workspaces 1 and 2 respectively.

5.1.9 Parameters

This command gives access to, and modification of, variables within the Eurotherm. The format of the command to change a parameter is:

    $ **CSET** parameter_name new_value

The values that can be changed are given in table 3.

Parameter name	Description	Units
prop	proportional band	percentage points
int	integral time	seconds
deriv	derivative time	seconds
power	maximum output power	percentage points
cycle	cycle time	seconds
setpoint	set-point value	kelvin

Table 3

Detailed information on the use of the above parameters is given in the following chapter.

6 TEMPERATURE CONTROL

Of the many parameters that can be varied in the Eurotherm temperature controller only five are important to enable efficient temperature control. In order of importance they are Proportional Band (P), Integral Time (I), Derivative Time (D), Cycle Time and Power output. A description of their functions is beyond the scope of this manual therefore only brief notes and some values of PID for certain common situations are given.

It is suggested that the cycle time remain at it's minimum setting of 0.1s. It is also generally recommended that the ratio of I:D should be ~5:1 and that P be in the range ~1.5-5% . The required PID values are best entered using the CAMAC system as described earlier, but it is also possible to enter values direct to the Eurotherm.

6.1 PID PARAMETERS

The subsequent values serve as guide-lines only and in all cases are strongly sample dependent. The heater power setting is also critical, generally it is preferable to set the heater power to the lowest value which will adequately maintain any given temperature change.

6.1.1 Orange Cryostat - directly heated sample

T (K)	P (%)	I (s)	D (s)
1 - 5	3	1	0.2
5 - 10	3	10	2

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10 - 20	1	10	2
20 - 300	1	50	10

6.1.2 <u>Orange Cryostat - cryostat heating</u>

T (K)	P (%)	I (s)	D (s)
0 - 20	2	40	8
20 - 50	2	100	20
50 - 150	2	200	40
150 - 300	2	1000	200

6.1.3 <u>R.A.L. Furnace</u>

T (°C)	P (%)	I (s)	D (s)
20 - 150	16	60	12
150 - 1000	16	30	6
1000 - 15000	16	¶_	-

¶ as the temperature increases the time constants should be progressively decreased.

6.1.4 <u>CCR (bottom loading)</u>

T (K)	P (%)	I (s)	D (s)
20 - 50	2	50	10
50 - 150	2	100	20
150 - 300	2	200	40

6.2 <u>USING A COMMAND FILE</u>

The main advantage of the instrument integrated CAMAC system is the ability to control and coordinate sample environment with the instrument

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running and data collection. This can be done by means of a DCL command file.

All instrument and CAMAC commands described so far may be issued from within a command file, along with some others shown below. The file is created using standard VAX/VMS editing techniques. By way of introduction a typical command file for variable temperature running is detailed below:

6.2.1 TEMP.COM - an example

```
! TEMP.COM                          ! Title "!" denotes a comment line
$ SET VERIFY                        ! to display on screen current command
$ CSET TEMP/RANGE=2 15              ! desired temperature is 15±1 K
$ CSET PROP 2                       ! setting PID's
$ CSET INT 40
$ CSET DERIV 8
!
$ BEGIN                             ! WAITING status veto will be active
$ WAITFOR 5000000 NEUTS            ! determines run length via monitor count
$ END
!
$ CSET TEMP/RANGE=2 25              ! desired temperature is now 25±1 K
$ CSET INT 100                     ! value of P remains at 2
$ CSET DERIV 20
$ WAIT 00:15:00
!                                   ! waits 15mins to allow equilibration
$ BEGIN                             !                    of temperature
$ WAITFOR 5000000 NEUTS
$ END
!
$ CSET TEMP/RANGE=2 35              ! desired temperature is now 35±1 K
$ WAIT 00:15:00
$ BEGIN
$ SET NOVERIFY                      ! in preparation to leave command file
$ EXIT                              ! returns command to the keyboard
```

To instigate the command file type:

```
$
$ @TEMP.COM <CR>
```

While the command file runs a $ prompt is not displayed and commands cannot be issued from the keyboard. To interrupt a command file, returning to keyboard control, type **<CTRL Y>**, that is hit Y while holding down the CTRL key.

It should be noted that for the successful completion of a command file operating over a wide temperature range, manual adjustment of the heating and/or cooling potential of the sample environment equipment will probably be required.

DATA ASSESSMENT

SECTION 3

1 THE ISIS COMPUTING SYSTEM - PUNCH

The current PUNCH system at ISIS in relation to HRPD is illustrated below in figure 10. The HRPD FEM (Front End Monitor) microVax(II) computer is linked to the main Vax8650 HUB computer via the Cambridge ring, an ETHERNET system permits the automatic transfer of raw data files after the completion of each run. From the HUB computer all data is archived, that is stored on magnetic tape or optical disk. Archived data is not directly accessible. In addition to the Cambridge ring the HUB computer also may be accessed via JANET (Joint Academic NETwork) .

Full analysis of HRPD data is possible using either the HRPD microVAX or the HUB computer from a local or remote terminal.

Fig 10   HRPD and the Punch system
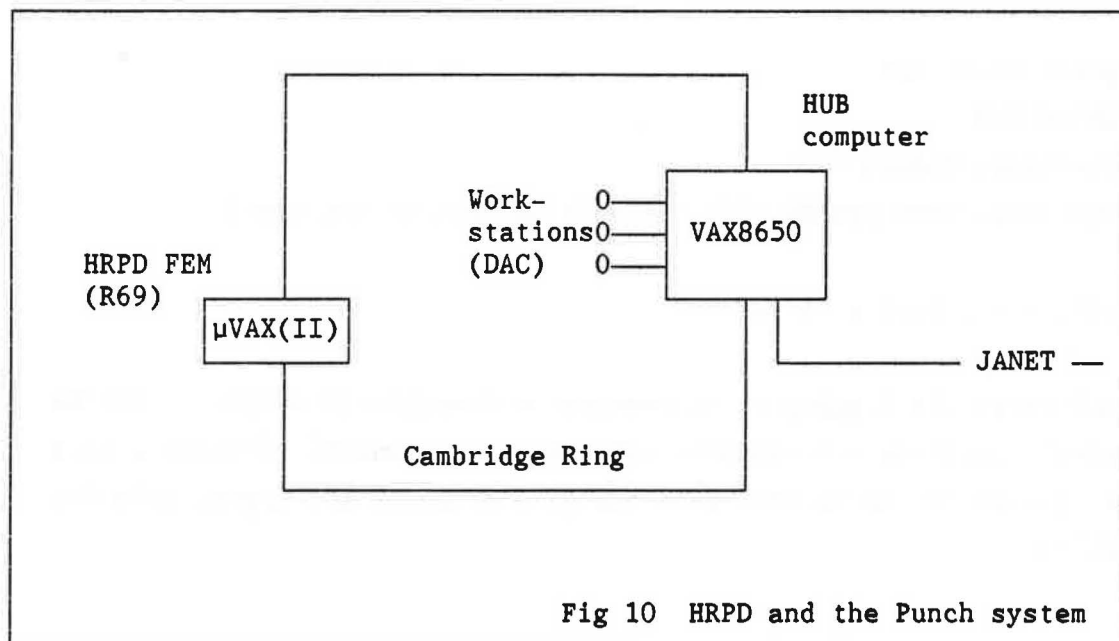
1.1 LOGGING ON

The initial stages of data analysis and viewing of data from a current run is normally carried out on the HRPD FEM. To log on the proceedure is as follows:

        press BREAK key
        DNS:C HRPD
        Username: HRPD <CR>
        Password: .... <CR> (this will change periodically)

This will then return a "*" prompt. It should be noted that when using a non-operator terminal in this manner the current run and raw data files cannot be affected.

For use on the HUB computer each research group will have a "user identifier" set up for them, the logging on proceedure is similar:

        press BREAK key
        DNS:C HUB
        Username: USER01 <CR>
        Password: OPEN_SESAME <CR> (this is defined by the user)

This will the return a "$" prompt.

In both cases the logging on proceedure automatically defines a series of default settings and commands relating to a central directory, this allows access to the various data analysis programs and appropriate raw data files.

2 DATA DISPLAY AND MANIPULATION - GENIE

GENIE is a data display and manipulation software package that is standard for all instruments at ISIS. A full explanation of GENIE is

available in the Punch User Guide (6) or the Punch GENIE Manual Version 2.3 (7). The GENIE program allows modification of experimental spectra such as the addition of spectra, background subtraction or normalisation with the facility to display at any stage. Other major features of particular use with HRPD data are model fitting and external user-definable functions.

This section deals primarily with the display and initial stages of analysis of HRPD data. Keyboard commands typed to the screen will be written in full with the shortest abbreviation shown in **bold** and capitalised.

2.1 USING GENIE

GENIE may be accessed via the HRPD microVax (do not use the operator terminal) or the HUB computer. The GENIE program is run as follows :

(log on)..
$ **GENIE**

>>.........(from this prompt GENIE commands may be issued)

The program contains a number of general WORKSPACES, a GRAPHICS WORKSPACE and a number of BUFFERS. In each work-space data relating to a single spectrum may be held. Data are held as arrays of x, y and e (ordinate, observation and error) values plus other parameters necessary for data interpretation and manipulation.

Running the GENIE program initialises a series of default settings concerning the location and subsequent retrieval of raw data files for inspection. Thus to assign a file to all work-spaces only the relevant run number and not it's location need be entered, eg. :

>>
>> **ASS**ign 999

```
>>
```

It should be noted that on the FEM microVax :

```
>> ASSign DAE
>>
```
and
```
>> ASSign CRPT
>>
```
are also permitted to allow direct access to the current run data in the data acquistion electronics (DAE) and the current run parameter table (CRPT).

2.2 THE FOCUS COMMANDS

Command files are set up to focus HRPD data, that is produce one average spectrum from the detector configurations defined by SPECTRA.DAT_25 and SPECTRA.DAT_90. The commands are simply:

```
>>
>> FOCUS <CR>
```
and
```
>>
>> FOC90 <CR>
```
respectively. The program will prompt the user for a run number or to enter DAE to view the current run. The appropriate sample position, 1 or 2m is also entered. The programs take a few minutes to run but automatically display the summed spectra. It should be noted that the focused data is temporarily stored in workspace 3 (W3).

Focused data may be stored by writing the appropriate workspace to a file. Eg:
```
>>
>> WRite/OPen W3 RUN0000.S20 <CR>
>> WRite/CLose <CR>
```

>>

It is essential to close the file (**WR/CL**) in order to save the spectrum
in a retrievable form.

The creation of a focused file is the first stage of data preparation
for Rietveld profile refinement. A previously stored file may be read
back for GENIE display by the following:

    >>

    >> **REad/OPen W3 RUN0000.S20** <CR>

    >> **REad/CLose** <CR>

    >> **Display W3** <CR>

    >>

2.3 THE PEAK COMMANDS

A variety of peak fitting routines are available all of which are run
using the PEAK command. The command may only be used when a spectrum is
currently displayed on the graphics screen:

    (graphics screen) <CR>

    >> **PEak Xmin Xmax** <CR>

    >>

The Xmin, Xmax limits may be set on the command line however the default
is to return the graphics cursor and allow on screen selection, by
hitting "L" and "U" to mark lower and upper limits respectively. This
basic peak command fits a linear background returning 0th, 1st and 2nd
moments of the remainder.

To use another routine simply insert the program name and it's location
on the command line, eg:

    (graphics screen) <CR>

    >> **PEak G:GEC Xmin Xmax** <CR>

    >>

Notes on the programs available are given below in table 4.

Program name	Modelled Peak function
G:GEC	Gaussian + exponential
G:CFVAN	Ikeda-Carpenter + Voigt
G:CGVAN	Ikeda-Carpenter +Gaussian
G:VOIGTVAN	Voigt

Table 4

2.4 GENERATING REFLECTIONS

It is often helpful to superimpose the expected Bragg reflections for a sample on the actual collected spectrum. The reflection listing is created by the program REFGEN using input parameters taken from a CCSL crystal data file as described below.

Three types of cards are needed for the crystal data file (<file_name>.CCL):

N card	(TITLE)	(optional)
C card	(CELL)	(required)
S card(s)	(SYMMETRY)	(required)

For example:

```
N    La2SrCuO6 (I4/mmm)
C    3.86   3.86   19.95
S    -X,-Y,Z
S    -Y,X,Z
S    -X,Y,-Z
S    -X,-Y,-Z
```

Having created the <file_name>.CCL file the reflection listing is generated by typing:

$ **REFGEN**

Coventionally the following nomenclature is used:

                Output file   : <file_name>.RLP
                Crystal data file   : <file_name>.CCL
                Reflections (TAG) file : <file_name>.TAG

The overall fightpath and 2 theta are 96.0505m and 168.329°, and 98.0398 and 174.020° for the HRPD 1m and 2m sample positions respectively. An appropriate minimum d-spacing should be chosen in Angstroms.

2.4.1 Displaying a TAG file

The TAG file may be displayed while in GENIE as follows:

        >> LOad Wn <file_name>.TAG G:LOAD
        >> Plot/Tag Wn y1 y2

Thus having displayed a spectrum the reflection tag lines are overplotted on the graph between the limits specified by y1 and y2.

2.5 GENIE KEYBOARD COMMANDS

Some GENIE commands are summarised below, again the command is written in full with the shortest abbreviation in bold capitals. In each case hit <CR> to return to a >> prompt from the graphics screen.

Alter
Binning : A bin grouping of 1 results in the display of every data point. The default value is 10.
    eg. >> A B 5   only every fifth data point is displayed.

Cursor : Switches on graphics cursor, hit **E** to exit. When the cursor is in operation (use ← → ↑ ↓ keys) single character commands may be typed. **X** displays the x-coordinate, **Y** displays the y-coordinate and **P** displays x- and y-coordinates.

Display : Displays spectrum in a specified workspace

HC : For laser print hard copy (R3 1.38).
HC1 : For laser print hard copy (R3 2.26).
HC2 : For laser print hard copy (DAC).

EXit : To leave the GENIE program.

Limits : To set new limits for the graph displayed.
    /X : To set x-limits eg. >> L/X 50000 70000
    /Y : To set y-limits eg. >> L/Y 0 250
    /D : Resets limits to xmin, xmax, ymin and ymax. (L <CR> will default to these settings).

Unit : To modify the units of a specified workspace.
    /D : converts to d-spacing in Å.

Zoom   : To blow up a selected portion of the plot. Opposite corners
               of the required area are defined by positioning the cursor and
               hitting any character key.

NEUTRON POWDER DIFFRACTION DATA ANALYSIS AT ISIS

SCIENTIFIC ASPECTS

SECTION 4

1 PROFILE REFINEMENT

1.1 THE RIETVELD METHOD

Until 1967, the refinement of powder diffraction patterns was carried out following the principles developed for single crystal diffraction, namely least squares refinement on |F| values based on structure factors extracted from the pattern. This approach has obvious disadvantages in a powder pattern where, due to the 1D nature of the pattern, in principle much of the information content is contained in overlapping peaks where accurate structure factor extraction may be difficult if not impossible. In his original papers developing the method (for constant wavelength neutron patterns), Rietveld (1967, 1969) introduced the idea of least squares fitting the entire diffraction profile without this intermediate extraction of structure factors or integrated intensities. By using to the full the possible information content of the diffraction pattern, the size of problems able to be attempted was expanded dramatically, and the accuracy of powder refinements increased. Today, most experiments carried out to give substantive structural information from powder samples exploit the Rietveld method of refinement and the application of the method has expanded from the original constant λ neutron work into X-ray studies, high resolution synchrotron studies, and into time-of-flight neutron powder diffraction pattern refinement on pulsed machines.

In the constant wavelength Rietveld method (with a Gaussian shape assumed for each peak) the function minimised is

$$\rho = \sum_i w_i (Y_i^{obs} - Y_i^{calc})^2 \ ,$$

where

$$Y_i^{calc} = \sum_k y_{ik} = \sum_k \alpha j_k L_k S_k^2 (2\sqrt{\ln 2}/H_k\sqrt{\pi}) \exp(-4\ln 2\{2\theta_i - 2\theta_k\}/H_k\}^2)$$

and $w_i = 1/\sigma_i^2$,

with

α = scale factor

$S_k^2 = F_k^2 + J_k^2$, the nuclear and magnetic contributions to the reflection

j_k = reflection multiplicity (no. of degenerate equivalents)

L_k = Lorentz correction

$2\theta_k$ = Bragg peak position

H_k = full width at half height ($= \sqrt{(U\tan2\theta_k + V\tan\theta_k + W)}$, assuming Gaussian peaks).

The summation for Y_i^{calc} is over all reflections contributing to point i on the diffraction pattern. For other application of the Rietveld method, such as t-o-f neutron diffraction, the details of the calculation of Y_i^{calc} will differ from the above, but the principle is the same as for the original formulation.

The "goodness-of-fit" of the refinement is normally measured by the four residuals detailed below

Weighted profile : $R_{wP} = \{ \sum_i w_i |Y_i^{obs} - Y_i^{calc}|^2 / \sum_i w_i (Y_i^{obs})^2 \}^{1/2}$

Profile : $R_P = (\sum_i |Y_i^{obs} - Y_i^{calc}| / \sum_i Y_i^{obs})$

Integrated intensities : $R_I = (\sum_k |I_k^{obs} - I_k^{calc}| / \sum_k I_k^{obs})$

Expected : $R_E = \{(N-P+C) / \sum_i w_i (Y_i^{obs})^2 \}^{1/2}$,

and the chi-squared parameter

$$\chi^2 = \{1/(N-P+C)\} \sum_i w_i (Y_i^{obs} - Y_i^{calc})^2 \{= (R_{wP}/R_E)^2\}$$

which is the natural measure of the fit, is normally minimised in the refinement. Therefore for a good fit, the weighted profile R-factor should approach the statistically expected R-factor value.

For time-of-flight neutron powder diffraction, certain of the terms in the Y_i^{calc} expression must be modified. These are notably the inclusion

of absorption corrections, since in t-o-f these are wavelength dependent and cannot be ignored as they can for constant wavelength diffractometers, the inclusion of wavelength dependent extinction corrections and a more complex peakshape, which will be discussed below.

1.2 PEAKSHAPES IN TIME-OF-FLIGHT NEUTRON POWDER DIFFRACTION

1.2.1 The combination of functions - Convolution

In general the shape of an individual Bragg peak in a t-o-f neutron powder diffraction pattern is a complex combination of several functions. The method of combination is that of convolution (or "folding") of the functions. The convolution, $c(\underline{u})$, of two functions $f(\underline{r})$ and $g(\underline{r})$ is defined as

$$c(\underline{u}) = f(\underline{r}) \star g(\underline{r}) = \int_{\underline{r}} f(\underline{r})g(\underline{u}-\underline{r})d\underline{r} \ .$$

Perhaps the most useful property of the convolution integral is the following. If $F(\underline{k})$, $G(\underline{k})$ are the Fourier transforms of $f(\underline{r})$, $g(\underline{r})$ respectively, then the convolution theorem states that the FT of the convolution $f \star g$ of f and g is the product of the individual FT's F and G. i.e.

$$FT\{f(\underline{r}) \star g(\underline{r})\} = FT\{f(\underline{r})\}.FT\{g(\underline{r})\} = F(\underline{k}).G(\underline{k})$$

or

$$C(\underline{k}) = \int_{\underline{r}} \{f(\underline{r}) \star g(\underline{r})\}\exp(i\underline{k}.\underline{r})d\underline{r} = \int_{\underline{r}} f(\underline{r})\exp(i\underline{k}.\underline{r})d\underline{r} \ . \int_{\underline{r}} g(\underline{r})\exp(i\underline{k}.\underline{r})d\underline{r} \ .$$

This property is obviously of great use if several possibly complicated functions have to be combined to form a peakshape, and its use will be demonstrated below.

1.2.2 Neutron time-of-flight peakshape

The peakshape in t-o-f powder diffraction is fairly complicated. This is due to several physical factors, notably the pulse shape, moderator physics, instrumental resolution and sample effects. Ignoring the latter, a reasonable approximation to the powder diffraction peak shape has been found to be

$$P(t) = \frac{t^2}{2\tau_f^3} \exp(\frac{-t}{\tau_f}) \star \{(1-R)\delta(t) + R(\frac{1}{\tau_s})\exp(\frac{-t}{\tau_s})\} \star \frac{1}{\sigma\sqrt{2\pi}} \exp(\frac{-x^2}{2\sigma^2})$$

where t = time of flight,

τ_f = fast decay constant,

τ_s = slow decay constant,

R = switch function, related to a Boltzmann function, $\exp(-E/E_o)$,

σ = Gaussian width parameter,

and * represents convolution.

The first two terms in this expression, representing the moderator physics (see below) were described by Ikeda and Carpenter (IC) (1985), based on results obtained from polythene moderators at IPNS, Argonne, USA.

1.2.3 Physics of the peak shape

As high energy neutrons emerge from the ISIS target, they meet a hydrogeneous moderator (95K liquid CH_4 for HRPD) and because of the high cross section of ^1H for neutron interactions, they undergo several collisions. In each collision of a high energy neutron with a proton, the neutron is likely to lose energy. Neutrons which escape the moderator material and into the beam tube during this "slowing-down" time are called epithermal neutrons. As a point of interest it is in the flux of these epithermal neutrons that a very high energy pulsed source such as ISIS is especially rich. The moderator effect on epithermal neutrons is to impose a fast exponential decay upon the peak shape, and this is characterised by the constant τ_f. Those neutrons which remain in the moderator until their energy has dropped sufficiently that they are essentially in thermal equilibrium with the moderator material (i.e. a neutron impacting a proton is as likely to gain energy as to lose it) are said to be thermalised. These thermal or Maxwellian neutrons have a characteristic decay constant which is much longer than that for the epithermal neutrons and is denoted τ_s. At short times (short λ, and hence higher energy neutrons), the epithermal component of the moderator contribution (τ_f) tends to dominate whereas at longer times the Maxwellian contributes most (τ_s). At intermediate energies, there is a switching region where the degree of contribution of each component can be described by a parameter (R) where R is the fractional contribution

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of τ_s, and $(1-R)$ that of τ_f.

The final term in the above equation represents the instrumental contribution to the resolution which is typically described by a Gaussian, describing the beam divergence, sample size and other effects.

1.2.4 Parameterisation of the peak shape

The parameterisation used in the programs GDELSQ and VDELSQ (see below) to describe the various peak shape parameters are detailed below :

switch (R) $\frac{1}{2}$ erfc $(a(b - 1/\lambda)$ (2 parameters)

fast decay (τ_f) $a + b\lambda$ (2 parameters)

slow decay (τ_s) $a + b\lambda$ (2 parameters)

Gaussian (σ) $(a + b\lambda^2 + c\lambda^4)^{1/2}$ (3 parameters)

Lorentzian (γ) $a + b\lambda + c\lambda^2$ (3 parameters) ,

where erfc is the complementary error function

$$\text{erfc } z = \frac{2}{\sqrt{\pi}} \int_z^{\infty} \exp(-t^2)dt \ .$$

The parameterisation used at present in the program VICLSQ (see below) is detailed below :

switch (R) $a_R/\{\exp(\lambda/b_R) + \exp(c_R^2/\lambda^2)\}$ (3 parameters)

fast decay (τ_f) $a_f + b_f\lambda + c_f\lambda^2$ (3 parameters)

slow decay (τ_s) $(a_s + b_s\lambda)$ erfc$(d_s(c_s-\lambda))$ (4 parameters)

Gaussian (σ) $(a_\sigma + b_\sigma\lambda^2 + c_\sigma\lambda^4)^{1/2}$ (3

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parameters)

Lorentzian (γ) $a_\gamma + b_\gamma\lambda + c_\gamma\lambda^2$ (3 parameters) ,

where erfc is again the complementary error function.

1.2.5 Physical rationale of the parameterisation in VICLSQ

Switch - The expression for the switch function represencts the harmonic
mean of terms representing absorption in the moderator $\{\exp(\lambda/b)\}$ and a
Boltzmann fraction term $\{\exp(-c^2/\lambda^2)\}$. As one can see from the form of
the switch function, $R = 1/(1/A + 1/B)$, for small A (i.e. short λ) the A
(absorption term) dominates whereas for small B (at large λ) B
dominates. The harmonic mean defines a function which satisfies these
criteria. The function used to describe R has been derived
semi-empirically from refinement of data from an MgO sample.

Fast decay - The parameters obviously describe the way the τ_f decay
varies with wavelength. In practice τ_f varies only as a function of λ,
and so the b_f term is the most important.

Slow decay - The slow decay constant τ_s has a fairly complicated
behaviour in the switching region between epithermal and thermal
neutrons, but at long λ shows no wavelength dependence. The
complementary error function has been found empirically to represent
this switching behaviour well, and the parameter a_s is relevant to the
magnitude of τ_s at long times. Again the erfc term is modelled from MgO
data.

Both the Gaussian and Lorentzian terms are associated with instrumental
and sample effects, with the instrumental effects being rather minor.

Sigma - The wavelength independent term a_σ is due to the finite width of
the neutron pulse emerging from ISIS ($\sim$0.4μs) and paracrystallinity in
the sample and is normally negligible. The $b_\sigma\lambda$ term includes the effect
of strain in the sample and a small contribution from the $\Delta\theta\cot\theta$ term in

the instrumental resolution, and is the most significant term in the expression for σ. The $c_\sigma\lambda^2$ term is a very small contribution due to particle size effects and stacking faults.

Gamma - As for σ, the a_γ term is due to paracrystallinity, but with no neutron pulse broadening. The minor $b_\gamma(\lambda)$ term is due primarily to strain in the sample and to instrumental effects. The instrumental contribution to the Lorentzian arise from the range of $\Delta\theta\cot\theta$ values arising from the 20 concentric rings of data collected from HRPD. When these are focussed in the standard way, the combination of Gaussian terms of different widths arising from rings of different radii lead to a contribution which can be adequately modelled by a Lorentzian shape, which is λ dependent since the component Gaussians are also λ dependent. The dominant term in the Lorentzian contribution is the $c_\gamma(\lambda^2)$ term arising from particle size and stacking faults.

The reason for the different styles of parameterisation of the σ and γ terms is that upon convolution, Gaussian widths add in quadrature ($\sigma_r^2 = \sigma_1^2 + \sigma_2^2$) whereas Lorenztians add linearly ($\gamma_r = \gamma_1 + \gamma_2$).

There are thus a total of 16 parameters available in this refinement program which are used to describe the peakshape, and in principle all of these can be refined. However, as discussed below, in any individual refinement only a limited subset of these 16 can justifiably be varied – the others are rigidly set by source and instrument characteristics.

The most commonly changed peak shape parameters (and those it is most valid to vary) are b_σ and c_γ, which should be adequate for the refinement of most patterns, including those with severe sample induced line broadening. To a lesser extent the sample dependent c_σ and b_γ may also be varied, but the contributions of these should be very small. Of the instrumental parameters, a_f, c_s and d_s and all of the switch parameters a_R, b_R and c_R are empirically determined and should NEVER be varied. The terms a_s, b_s and b_f can in principle be varied in the most accurate refinements but this should be done with extreme caution and

avoided unless the accuracy warrants it. These rules are summarised below (with parameter names used in the refinement programs in brackets) :

Commonly varied (sample)	b_σ (SIGM 2)	c_γ (GAMM 3)	
Small sample contributions	c_σ (SIGM 3)	b_γ (GAMM 2)	
Variable instrument parameters (with caution)	a_s (TAUS 1)	b_s (TAUS 2)	b_f (TAUF 2)
Fixed parameters (empirical)	a_f (TAUF 1)	c_s (TAUS 3)	d_s (TAUS 4)
	a_R (SWCH 1)	b_R (SWCH 2)	c_R (SWCH 3).

1.3 PROFILE REFINEMENT PROGRAMS - DISCRETE FOURIER TRANSFORM TECHNIQUES

1.3.1 Profile refinement programs - GDELSQ, VDELSQ

The stock profile refinement program for ISIS powder diffraction data is at present the program GDELSQ (Gaussian-Double-Exponential Least SQuares) which has as its peak shape the convolution of a Gaussian with two decaying exponential functions representing the fast and slow contributions of the moderator. Also available is the program VDELSQ (Voigt-Double Exponential Least SQuares) which is GDELSQ with a Lorentzian component added. The Voigt function used in VDELSQ is a convolution of Gaussian and Lorentzian functions

$$V(u)=G(x,\sigma)*L(x,\gamma)= \int_x Aexp(\frac{-x^2}{2\sigma^2}) \ \frac{A'}{1 + \gamma(u-x)^2} \ dx$$

The refinement programs GDELSQ and VDELSQ are restricted to 30000 reflections and 250 refinable parameters.

1.3.2 VICLSQ - profile refinement using FFT techniques

In the most complex parameterisation available to date, the weighted double decaying exponential, a Gaussian and a Lorentzian component have been incorporated into the program VICLSQ (Voigt-Ikeda-Carpenter Least SQuares), where the convolution is between the Ikeda-Carpenter function described above with the Voigt (Gaussian-Lorentzian) function. These peak shape calculations employ Fast Fourier Transform (FFT) techniques. This has considerably more flexibility in that in principle it allows any desired function to be folded into the peak shape numerically.

In practice the analytical Fourier Transforms of each peak shape function are evaluated and these transformed functions are then multiplied together in Fourier space. The back transformation of the (by now very complicated) product function is carried out numerically.

1.3.3 Dealing with function discontinuities - Eagle's Method

There is a problem with this type of calculation in that the FT of a Lorentzian consists of two abutted exponentials and hence there is a

discontinuity in the FT function if evaluated discretely. Several techniques are available with discrete Fourier Transforms which endeavour to use numerical approximations to avoid such problems (Champeney 1973). One method which we have investigated (Eagle method) and broadly speaking consists of using using linear combinations of relevant piecewise continuous polynomials and their derivatives in order to express the FT adequately. Such a linear combination of functions can be shown to be well behaved under the imposed conditions. The basic principle satisfied by using Eagle's method is to try to make the discrete FT look as akin to the continuous (analytical) FT as possible, thus minimising discontinuity problems, without a massive increase in calculation time. There are other methods for dealing with discontinuities including polynomial and spline interpolations.

1.3.4 Improving the evaluation of discrete FT's – Richardson's Extrapolation

In order to improve the agreement between an analytical solution and the discrete FFT technique we have used to back-transform the peak shape function, we use Richardson's extrapolation (Champeney 1973). This essentially consists of evaluating the discrete FT several times, using different sampling increments Δ_1, Δ_2, Δ_3 etc. where the whole pattern consists of N_1 steps of width Δ_1, or N_2 steps of width Δ_2 etc. and combining the FFT's calculated using these different numbers of sampling points. For Richardson's extrapolation to remove an error of the order $1/N^2$, one calculates the discrete FT for two values of N, $N_1 > N_2$, and combine these in the expression

$$FT(R) = \alpha_1 \cdot FT(N_1) + (1-\alpha_1) \cdot FT(N_2)$$

where

$$\alpha = N_1^2 / (N_1^2 - N_2^2)$$

so that if one chooses $N_1 = 2N_2$, $\alpha = 4/3$ and Richardson's extrapolation is

$$FT(R) = 4/3 \, FT(N_1) - 1/3 \, FT(N_1/2)$$

To remove terms of order $1/N^4$ in addition, one must calculate three discrete FT's ($N_1 = 2N_2 = 4N_3$) and use the extrapolation relation

$$FT(R) = 64/45 \ FT(N_1) - 20/45 \ FT(N_2) + 1/45 \ FT(N_3) \ .$$

The choice of which (if any) degree of Richardson's extrapolation to use is at present hard-wired into the code but it is hoped to include this as a parameter if it is found to be important. The CPU requirements of VICLSQ obviously increase considerably if a Richardson's extrapolation is used in the peak shape calculations.

1.3.5 The use of the Lorentzian term – Line Broadening

With the extremely high intrinsic instrumental resolution of HRPD, frequently the accuracy of a powder diffraction experiment on the instrument is restricted by the sample quality. This is not statistical accuracy – one traditionally considers that improved experimental accuracy can be achieved through the medium of increased counting times or sample size and hence improved statistics – but rather some fundamental microscopic property of the sample which manifests itself in the **shape** of the Bragg peaks.

This normally consists of a broadening of the peaks in the pattern, caused by some imperfection in the crystal (Warren, 1969). In general the shorter the spatial extent of the imperfection within the crystal, the larger its effect on the peak shape. For example "particle-size" broadening is caused by the finite extent of the coherently diffracting domains within a crystal (the broadening does not give the crystallite size of the powder "granules" since these will rarely consist of a single domain).

It can be shown, by analysis of the effect of small crystallite (domain) size on the diffraction maxima (via the Laue equations), that the effect of such imperfections is to introduce a Lorentzian term into the peak shape expression. This is often very apparent in severely broadened patterns, since the Lorentzian has a very characteristic shape, with extended "tails" which cause the peak to flare out somewhat away from its centre. In a case where such an effect is obvious, it is essential to include a Lorentzian component in the peak shape description for

refinement to be accurate.

Particle size broadening tends to broaden peaks fairly indiscriminately, with the broadening increasing as λ increases, but there are other crystal imperfections which can lead to more complex line-broadening effect. These can be manifest, for example, in specific broadening of say the (h00) reflections in a particular pattern, and this obviously gives information on some directional distortion within the material. This could well represent an anisotropic strain in the crystal, or some twinning boundary effect, or a stacking fault direction. The separation of individual contributions to line broadening is not easy in profile refinement, and one would normally require some prior knowledge of the relevant physical model (or good guesswork) in order to achieve quantitative results from the experiment.

2 GENERAL CONSIDERATIONS

2.1 AUTOINDEXING AND CELL DIMENSION DETERMINATION

If there is a truly unknown structure under study in a powder
diffraction study, there is a logical sequence of investigations to be
followed before the structure can be solved or refined. The first is to
test the sample for purity by some chemical or other means and the
second to ensure that a crystalline diffraction pattern is obtained!

Once these have been verified as far as possible the diffraction pattern
should be recorded, obviously as accurately as possible. For a
completely unknown structure the next thing required is to find the unit
cell and hence to index the pattern. If the cell parameters are
approximately known, then a comparison of expected and measured
d-spacings can be made and a least-squares procedure followed to refine
the cell. At present this is done in the program CELLSQ which requires
as input a list of reflections with their associated time-of-flight and
will output a refined unit cell. One point which should be noted here is
that the quantities used in cell dimension refinements are not the cell
parameters $(a,b,c,\alpha,\beta,\gamma)$ themselves but rather quantities related to
their reciprocal space counterparts as detailed below :

$$A^* = a^{*2} \; ; \qquad D^* = 2b^*c^*\cos\alpha^* \; ;$$
$$B^* = b^{*2} \; ; \qquad E^* = 2c^*a^*\cos\beta^* \; ;$$
$$C^* = c^{*2} \; ; \qquad F^* = 2a^*b^*\cos\gamma^* \; .$$

If no unit cell is known the powder diffraction pattern can still be
used to determine the unit cell, once a list of d-spacings is known.
Many modern autoindexing routines rely on the simplified relations
between d-spacing and the above cell parameters expressed in reciprocal
space

$$1/d^2 = h^2A^* + k^2B^* + l^2C^* + klD^* + lhE^* + hkF^* \; .$$

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The reliability of autoindexing routines rely crucially on the accuracy of the extracted d-spacing data - even small errors in these can lead to severe difficuly in determining the correct cell.

There are two general categories of modern autoindexing routines - those working in "index" space (where the Miller indices (hkl) are varied) and those working in "parameter" space (where the cell parameters are varied). There are also two types of method used - "deductive" methods where one attempts to infer likely cell parameters from relations between observed positions and "exhaustive" where one scans systematically through the relevant solution space searching for good agreement. Examples of the deductive method are the Visser (1969) program (FZON) and of the exhaustive method, TAUP in parameter space and TREOR (Werner,1984) , KOHL in index space. For very high symmetry spaces, graphical methods can sometimes yield results, and the early methods were based on this type of procedure.

The difficulties encountered by autoindexing programs, especially for low symmetry (triclinic, monoclinic) structures cannot be overstressed. It is absolutely essential to extract accurate d-spacing data for, say, the 20 highest reflections. Sometimes missing reflections may not seriously impair the finding of a solution, as long as there are not too many of the low index reflections missed, but inclusion of any spurious peaks can cause serious problems. Providing one has an accurate and complete list of d-spacings, autoindexing should be successful in some 80% or so of cases. Many of these autoindexing programs are available to users at ISIS, accessible through the command INDEX, running a flexible command procedure dealing with the facilities available.

2.2 THE USE OF CHEMICAL CONSTRAINTS IN PROFILE REFINEMENT

Although the advent of Rietveld refinement techniques has increased substantially the size of problems able to be attempted using powder diffraction techniques, there remain many problems in which the number of parameters is so great as to cause serious difficulty. Typical of such materials are zeolites, other clathrate materials and large scale organic / biological molecules. Since any least squares refinement procedure must be overdetermined (No. of observations > No. of variables) in order to function well, attempting to refine for example, all atomic coordinates, anisotropic temperature factors, site occupancies etc. in such large scale materials can often lead to severe problems related to underdetermination of the problem.

There are two obvious ways in which the problems of underdetermination can be reduced (Pawley, 1972) : increasing the number of observations and/or reducing the number of variables. Given that the experimental data collection from a particular material has been as careful and comprehensive as possible, there is no way to increase the number of reflections available, and so the extra observations have to come from some other source. In addition, to reduce the number of variables simply by ignoring a selected few is somewhat unsatisfactory and substantially reduces the generality of the refinement. Thus a method of reducing the number of variables in the refinement without reducing the number of physical variables present should be found.

2.2.1 Increasing the number of observations - Slack Constraints

Assuming that one has a model for the structure under study, and that a reasonable amount of chemical knowledge is available, then by imposing some of this knowledge upon the refinement one can achieve the desired increase in observations. Frequently these slack constraints are related to bond lengths, and it is in terms of these that the discussion will proceed.

Essentially a slack constraint is distinguished from a strict constraint

(which are discussed below) by being a condition which is obeyed to within some predetermined limit. For example if a particular bond length in a molecule under study is constrained to be $R_i \pm \sigma_i$ and the refinement produces a value r_i for this parameter, then there is an additional term in the function to be minimised in the least squares process, namely

$$\sum_{\underline{h}} w_{\underline{h}} \{(F_{\underline{h}}(obs) - F_{\underline{h}}(calc)\}^2 + \sum_i w_i (r_i - R_i)^2 .$$

As can be seen from this expression, the inclusion of this type of bond length constraint has formally the same effect as increasing the number of "actual" observations, in this case the structure factors $|F_{\underline{h}}(obs)|$. The relative importance of these two types of observation is governed by the weights $w_{\underline{h}}$ and w_i. The weights w_i of the constraint terms are governed by the value σ_i given for the allowed deviation of the parameter. The above equation is the formal expression of why slack constraints increase the number of observations independent of the diffraction experiment. Slack constraints are dealt with locally using the L SLAK commands in CCSL.

2.2.2 Reducing the number of variables - Strict Constraints

In strict constraints, essentially what one does is to relate the variations of a series of variables together in some way, so that the least squares refinement deals with a group of parameters as one variable. Examples of this procedure are inclusion of rigid groups where the refinement of one atom sets the values of several others, symmetry constraints where a molecule is restricted to have a particular symmetry, imposition of an overall temperature factor, imposition of a single temperature factor for a particular atomic species, relation of site occupancies to satisfy stoichiometric requirements and for use in disorder studies, etc. These constraints are conceptually very simple but can have a tremendous effect on a particular refinement. Judicious use of strict constraints can force an apparently intractable problem into a satisfactory refinement path. Locally strict constraints are governed by L RELA commands in CCSL.

2.3 ALTERNATIVES TO PROFILE REFINEMENT - CAILS, GRILS

In cases of severe difficulty when all attempts at profile refinement
fail then one must revert to techniques not specific to powder
diffraction. These techniques, as mentioned earlier, involve the
extraction of structure factor data from the diffraction pattern and the
use of these structure factors in traditional crystallographic
techniques.

2.3.1 The extraction of intensities for unknown structures

Given that the unit cell of the material under study is known, but that
no information is available about the structure, then obviously no
structural refinement can be carried out (no model means no F_h(calc)
values). However, knowledge of the unit cell enables one to predict the
positions of expected peaks in the pattern and this information can be
exploited to extract useful intensity information from the pattern
(Pawley, 1981).

In the CAILS (Cell And Integrated intensities Least Squares) procedure,
one attempts to refine both the unit cell dimensions (via accurate
location of the peak positions at each predicted point) and also the
intensities of the peaks found at each predicted reflection position.
The variables in the refinement thus tend to be the cell parameters and
the resolved integrated intensities in the pattern. The resolution of
the pattern is a variable which can be input to the program - any
reflections whose predicted positions are closer than some limit are
regarded as overlapping and assigned as degenerate reflections
contributing to the same intensity. Once the integrated intensities are
extracted using CAILS, structure factors can be generated and used in
attempted structural solution, $|F|$ refinements etc.

Since for unknown structures a cell can frequently be available, the
ability to extract accurate intensities can be crucial to the subsequent
application of the information in the diffraction pattern to the
extraction of structural information. The application of the CAILS

technique allows a flexible method of using the known information (unit cell and observed diffraction pattern) to attempt to optimise the extraction of unknown information (integrated intensities → structure factors → structure).

2.3.2 The extraction of intensities for known structures

As stated above, profile refinement is not always possible even if a good model structure is available, perhaps due to problems with peakshape, or multiple phases etc.). The obvious course to pursue if this is the case is to extract $|F_h|$ values from the pattern and use single crystal refinement procedure. However, one must always bear in mind that what we have performed is not a single crystal experiment but one of powder diffraction with its associated potential for information loss. Of course, once the list of structure factors is available the subsequent programs are to a large extent indifferent as to how the data were originally collected. It is in the extraction of structure factors that the unique problems of powder diffraction must be dealt with.

As in the CAILS technique above, the fundamental principle of the GRILS (GRouped Intensities Least Squares) method is to recognise that in a powder pattern there is a limiting resolution defining a separation below which two peaks cannot be separated but must be considered to be contributing equally to the observed intensity. The input of a list of reflections believed to be contributing to a particular diffraction peak, along with the knowledge of the structure factors (and hence the intensity contribution) of these reflections individually, allows accurate extraction of intensities from each peak, and the breaking down of this into individual reflection contributions. Thus a complete list of individual structure factors for each reflection contributing to the pattern can be extracted, which in principle is as complete as an equivalent list from a single crystal experiment. Subsequent manipulations are then based on as full a list of $|F_h|$ values as possible.

2.3.3 The unequal apportioning of intensities of overlapping reflections

For an unknown structure for which a powder diffraction pattern has been measured, traditionally intensities have been apportioned equally to the individual contributing reflections in a degenerate peak. This degeneracy may be true (two reflections with exactly the same d^*) or resolution induced (two reflections with a d^* separation beyond the resolution of the pattern). The apportioning of equal intensities in this way can have a severe effect on the accuracy of the extracted structure factor list, allowing for both the underestimation of very strong reflections and the overestimation of very weak ones. For structural solution attempts, both of these inaccuracies can have very serious consequences (see below) and it is of obvious benefit to try to improve this division by some method.

Two methods have recently been described of doing this, with a fair degree of success apparent from both techniques (David, 1986). The first involves an adaptation of the equations involved in Sayre's squaring method, to provide the equivalent of the triplet etc. relations used in direct methods of structural solution which in turn provide a probable estimate of the relative contributions of individual reflections to a degenerate peak. The second method is based on maximum entropy techniques providing an estimate of these intensities based on the production of smooth Patterson maps. The exploitation and improvement of such techniques will lead to more reliable structure factor lists being available from powder patterns for unknown structures.

2.4 STRUCTURAL SOLUTION FROM HRPD DATA ("AB INITIO")

The subject of structure determination from powder diffraction patterns has recently been the focus of considerable interest (David, Johnson and Wilson, 1987), since it is only with the advent of very high resolution instruments that the technique has become feasible. The primary problems in solving crystal structures in this way are the lack of information available, especially at lower d-spacings, and the intrinsic degeneracy of reflections with identical d-spacings. The first of these is the problem which has to some extent been mitigated by improved resolution, allowing the resolution of peaks which previously would have been considered to be overlapping and hence the extension of the data set. Data are extracted by a technique such as CAILS (since we are dealing with an unknown structure) to provide a list of structure factors which are as accurate and complete as possible. For the second problem there is no instrumental solution since these truly degenerate reflections are inseparable (unless one of them is excessively broadened, for example, which would lead to an anomalous peak shape which may be interpretable in terms of the relative intensities of the constituent reflections) and some other technique is required if these are to be apportioned anything other than average intensity values. These possible other techniques are mentioned above.

Assuming that the best possible list of reflections and structure factors has been obtained, the problem becomes one of standard structure solution and will exploit the techniques developed for the solution of single crystal structures. The problems posed by a powder determination mean that the standard methods are in general at the limits of their feasibility. The problems able to be attempted in this way are somewhat limited in complexity at present, but undoubtedly the scope will increase in the future as more experience is gained in the field. Structure determination from powders is, however, unlikely to become nearly so widespread or as widely applicable as single crystal work, and many problems will remain intractable which are relatively straightforward if a sizable crystal can be obtained.

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2.4.1 <u>Structural determination techniques</u>

To adequately describe these is beyond the scope of this manual but a brief summary of the techniques is given below. The fundamental problem of structural determination is that the experimental intensity data I_{hkl} contain no information on the phases of the diffracted radiation (the "phase problem"). Structural determination techniques endeavour to provide this missing phase information to allow for the construction of a Fourier map (see below) representing the scattering density.

2.4.2 <u>Direct Methods</u> - in direct methods probabilistic relations between the phases of the strongest reflections are derived and used to provide phases for an ever-increasing subset of the observed reflections, based on a small starting set of reflections with known or assumed phases. In a multisolution approach typified by the MULTAN routines (also incorporated within the MITHRIL program) (Gilmore, 1984) rapid calculations are made of many possible phase paths based on several possible starting phase sets and the best of these frequently lead to elucidation of the structure. Direct methods are the most widely used structure solution technique today.

2.4.3 <u>Patterson methods</u> - the Patterson function is a Fourier summation calculated using the I_{hkl} as coefficients and thus phases are not required. The resulting map, however, represents not the scattering density $\rho(\underline{r})$ but the convolution of this with its centrosymmetric inversion, $\rho(\underline{r})*\rho(-\underline{r})$. Peaks in the Patterson map do not therefore represent atoms but rather interatomic vectors, which leads to a major problem in unravelling the vector map into an atomic map.

Interpretation of a Patterson map is normally performed in one of two ways :

(i) Heavy atom method - if a small number of heavy atoms are present in the structure, the vector in the Patterson map representing the interatomic separation of these will be dominant and hence the location of the heavy atoms can be found. This information is frequently sufficient to lead to structural solution. In neutron experiments,

however, there are few species which dominate the scattering in this way;

(ii) Model superposition - if the expected stereochemistry of the unknown structure is known, then by comparing the observed Patterson function with that calculated from the model, one can obtain the orientation and position of the model within the unit cell and hence solve the structure. These calculations can be performed either in real space, where the Patterson map is calculated, or in reciprocal (observation) space, where the model molecular transform is compared with the transform of the Patterson function, consisting simply of the $|F_{\underline{h}}(obs)|^2$ values.

2.4.4 Problems specific to powder methods

Many of the problems found with structure determination using powders are related to the lack of resolved data and in the neutron case, due to the fact that most structure solving codes are optimised for use with X-ray data and may require rewriting to make them compatible with neutrons (Wilson, 1987).

When there is a very limited data set of reliable intensities, the number of phase relationships available for direct methods may be very small, and thus the phasing path is curtailed and inaccurate. In addition, the calculation of Fourier maps based on a very small number of Fourier coefficients can lead to poor scattering density maps and hence to incorrect atom location. The overestimation of possibly weak reflections and the underestimation of strong ones using the equipartition of intensities in overlapping peaks can lead to problems in phasing and again in the calculation of Fourier maps. Patterson methods tend to be more tolerant of incomplete or inaccurate structure factor lists, but even these need a reasonable set of reflections.

2.5 FOURIER MAPS AND FOURIER REFINEMENT TECHNIQUES

The fundamental purpose of most structural work is to end up with a set of atomic positions which accurately represent the scattering density within the crystals, and to have refined other parameters concerned with the atoms (temperature factors, site occupancies etc.) such that the agreement between the observed and calculated sets of structure factors is as good as possible. This optimised set of structure factors can be used to reconstruct the scattering density present by performing a Fourier summation using the $F_{\underline{h}}(calc)$ as coefficients. It is to be remembered that the $F_{\underline{h}}(calc)$ from the model contain both magnitude and phase information, where the $|F_{\underline{h}}(obs)|$ contained only magnitude, i.e.

$$F_{\underline{h}}(calc) = |F_{\underline{h}}(calc)| \exp\{i\alpha_{\underline{h}}(calc)\},$$

where $\alpha_{\underline{h}}(calc)$ are the phases.

The Fourier synthesis used to reconstruct the scattering density $\rho(\underline{r})$ is

$$\rho(\underline{r}) = \sum_{\underline{h}} F_{\underline{h}}(calc) \exp\{-2\pi i\underline{h}\cdot\underline{r}\} = \sum_{\underline{h}} |F_{\underline{h}}(calc)| \exp\{-2\pi i(\underline{h}\cdot\underline{r}) + \alpha_{\underline{h}}(calc)\}.$$

The map produced using this summation is called simply a Fourier map or an "F(calc)" Fourier. It is used to illustrate the scattering density resulting from the atomic parameters currently used to construct the $F_{\underline{h}}(calc)$ values.

2.5.1 Fourier recycling - the F(obs) Fourier

At an earlier stage in the refinement procedure there are two forms of Fourier synthesis which are of more use than the F(calc) Fourier. The first of these is the F(obs) map which is used in Fourier recycling procedures. The F(obs) map is calculated using

$$\rho(\underline{r}) = \sum_{\underline{h}} |F_{\underline{h}}(obs)| \exp\{-2\pi i(\underline{h}\cdot\underline{r}) + \alpha_{\underline{h}}(calc)\} .$$

Note the use of $\alpha_{\underline{h}}(calc)$ in this synthesis since $\alpha_{\underline{h}}(obs)$ does not exist! Often an F(obs) Fourier is used when a significant part of a structure

is still missing from the model. By using the best available set of calculated phases α_h along with the observed structure factors, often the missing atoms will appear as peaks in the map. Developing a structure by adding atoms in this way is called Fourier recycling for obvious reasons. Often in a structure determination the initial model used for phasing an F(obs) Fourier is very inaccurate but contains sufficient information to lead to more information being revealed which can then be used to improve the phases for subsequent calculations.

2.5.2 The Difference Fourier

When a structure is approaching completion and only a small part of the molecule remains undefined, the simplest way of locating the remaining atoms is to calculate a difference Fourier map. This map, calculated using

$$\Delta\rho(\underline{r}) = \rho(obs) - \rho(calc)$$

$$= \sum_{\underline{h}} (|F_{\underline{h}}(obs)| - |F_{\underline{h}}(calc)|) \exp\{-2\pi i(\underline{h}.\underline{r}) + \alpha_h(calc)\} ,$$

$$= \sum_{\underline{h}} (\Delta F_{\underline{h}}) \exp\{-2\pi i(\underline{h}.\underline{r}) + \alpha_h(calc)\}$$

should in principle produce as its main features those aspects of the scattering density contained in the $F_h(obs)$ which are not yet manifest in $F_h(calc)$, since by this stage the α_h ought to fairly accurate. The coefficients $\Delta F_{\underline{h}}$ are often termed the difference structure factors.

A typical use of difference Fourier calculations is to determine hydrogen atom positions in a structure once the remaining atoms have been adequately refined. In this respect neutrons have both advantages and disadvantages over X-ray calculations. The advantage is that since hydrogen scatters neutrons at about the same strength as other atomic species, the troughs {ρ (b) is negative for hydrogen with neutrons} should be very apparent in the difference map. For X-rays often the hydrogen atoms can remain obscured in a ΔF map. The disadvantage is that the phases used to calculate the difference Fourier are less accurate than for the X-ray case, for precisely the same reason – the unknown

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atoms (hydrogen) contribute significantly to the overall scattering from the material in the neutron case and so α_h values calculated without hydrogen atoms being included will tend to be less accurate.

2.6 ABSORPTION AND EXTINCTION CORRECTIONS

In t-o-f neutron powder diffraction, both absorption and extinction are somewhat more complex to deal with than in the constant wavelength case, as a result of their strong wavelength dependence.

2.6.1 Absorption

Absorption is the attenuation of a beam of radiation as it passes through the sample, due to any scattering or absorption process which does not contribute to the quantity being measured. The absorption correction for neutron diffraction can be written in general terms as

$$A = (1/V) \exp\{-N\sigma(p_1 + p_2)\}dV$$

where A is the attenuation of the beam through the sample, V is the sample volume, N is the number of units per unit volume, p_1+p_2 is the total path length of the diffracted beam through the sample, and σ is the cross section of each unit. The wavelength dependence arises because $\sigma = \sigma\{E(\lambda)\}$. The absorption correction normally applied in crystallography in backscattering geometry is

$$I = (I^0/2\mu x) \{1 - \exp(-2\mu x)\} ,$$

where $I_0(\lambda)$ is the incident intensity (unattenuated), x is the path length through the sample, $\mu(\lambda)$ is the absorption coefficient and I the observed intensity. For a particular Bragg reflection therefore

$$I_{hkl} = \{I^0_{hkl}/2\mu(\lambda)x\} \{1 - \exp(-2\mu(\lambda)x_{hkl})\} .$$

The absorption correction as applied is of the $1-\mu(\lambda)x$ to first order, and the coefficient μ is a variable parameter. Under normal circumstances for a powder of randomly oriented crystallites, all the x_{hkl} are the same and so an absorption correction is not required. It is the appearance of the $\mu(\lambda)$ wavelength dependent absorption coefficient which renders the correction necessary. One final point is that neutrons

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are much less heavily absorbed than X-rays, and so the corrections tend to be less severe for experiments carried out using the former radiation. The L ABSC command is used to apply absorption corrections.

2.6.2 Extinction

Primary extinction is caused in "perfect" crystals where destructive interference from multiple Bragg reflections from sets of parallel planes reduces the diffracted intensity. Secondary extinction results from the secondary Bragg reflection of a diffracted beam back into the incident beam direction by a mosaic block of identical orientation within the crystal. For a polycrystalline material with random orientations of mosaic blocks, the effects of secondary extinction tend to be manifest in diffuse scattering rather than in the Bragg peaks.

The effect of extinction is to reduce the intensity of Bragg peaks, especially the strong ones, where the "multiple" reflections have more appreciable intensity. If we define the extinction coefficient e as the ratio

$$e = \frac{\text{Observed Integrated Intensity}}{\text{Kinematic Integrated Intensity}}$$

then an appropriate correction can be applied to the calculated intensity (and hence the calculated profile point magnitude) in the refinement calculation by multiplying by e (< 1.).

The extinction correction is carried out in the profile refinement calculations in the form (Sabine, 1985)

$$e = (1 + x)^{-1/2} ,$$

where $x = (3/4 \ N_c F_{hkl} \lambda D)^2$,

with N_c = number of cells in the crystal,

   F_{hkl} = structure factor magnitude,

   λ = wavelength,

   D = grain diameter.

As can be seen from the above, the extinction correction is wavelength dependent and hence is more complicated for t-o-f than for constant wavelength experiments. In spite of this, the above expression has been found to deal well with the correction in neutron t-o-f powder diffraction studies. In practice, the parameter varied in the least squares procedure in the profile refinement is D, the grain diameter. This parameter typically has dimensions of the order of a micron $(10^{-6}$m), and the parameter on the L EXTN card in the input file is expressed in units of microns.

2.7 PREFERRED ORIENTATION

In a powder sample consisting of non-isotropic crystallites, the geometrical distribution of these crystallites is often non-random. For example, for plate-like crystallites in a flat plate sample, it may be expected that the crystallites will orient preferentially with the crystallite flat planes parallel to the sample flat plane. Similar arguments hold for rod-like crystallites in a cylindrical geometry sample. This effect is called preferred orientation, and obviously leads to intensity variations within the diffraction pattern depending strongly on the sample orientation in the beam.

The factors which influence preferred orientation are: sample preparation techniques - how the crystallites are grown, how the bulk sample is prepared from these i.e. by compression or by spinning etc.; sample geometry i.e. whether plate, cylinder etc.; sample geometry within the beam, more generally data collection geometry; any external influences on the sample while data collection is taking place, e.g uniaxial pressure. In contrast to X-rays, for most neutron powder diffraction samples the extent of preferred orientation is rather small and refinements do not always take the effect into account. However, in many cases the refinement is inadequate and gives a poor fit unless some correction is performed.

Preferred orientation corrections take the form of pole-density distributions, which essentially measure the density of (hkl) reflections from a powder sample as a function of the preferred orientation direction (HKL). Obviously if the reflection geometry is such that the (HKL) preferred orientation direction is in a position to diffract into the detector, the intensity measured for the (hkl) reflections where (h=H, k=K, l=L) will be enhanced by some factor over, say, the (h=2H, k=-K, l=3L) reflections. It is the correction of diffracted intensities for this kind of effect that is the purpose of preferred orientation corrections.

The form of the pole-density distribution has been modelled in several ways, most simply by Gaussian functions. The correction used here is based on the March model (Dollase, 1986; March, 1932), derived from a theory describing grain rotation in a powder sample, which produces preferred orientation. The degree of preferred orientation is described by a single refinable parameter r, the March coefficient. The March model can deal with both plate-like and rod-like crystallite geometry, with the variable r showing different behaviour for each case. For plate-like crystallites, $r = d/d_0$, where d_0 is the thickness of a random sample, and d the thickness after application of the effect causing preferred orientation. In the case of rod-like crystallites the relation is $r = d_0/d$. The March distribution describing the pole-figure distribution for a cylindrically symmetrical specimen where some stress has been applied along the cylindrical axis during sample preparation is given below

$$P(r) = (r^2\cos2\alpha + (1/r)\sin^2\alpha)^{-3/2} \, ,$$

where α is the angle between the (HKL) direction of the plates and the (hkl) reflection.

In samples showing severe preferred orientation the parameter r can be as small as ~0.5, representing an equivalent sample compaction of about 50%. The correction of reflection intensities for this magnitude of preferred orientation effect would be absolutely crucial for the achievement of an adequate refinement. As stated above, most neutron diffraction experiments do not suffer significantly from this effect, but it is as well to be aware of the possibility and to have the capability of making the appropriate corrections. The preferred orientation correction is built into the profile refinement codes at ISIS.

2.8 THE PROBLEMS OF TEMPERATURE FACTOR REFINEMENT

Since the accuracy of thermal parameter refinement in neutron powder diffraction depends to a large extent on the background removal, there has been much effort expended in improving the latter. Background removal by eye is in general unreliable and can lead to inaccurate thermal parameters. A more correct and useful technique is to fit a polynomial to the background, which is straightforward given a smoothly varying background function. In the profile codes at ISIS, an nth order Chebyshev polynomial is fitted, with in most cases n=5 being adequate for a very good fit. For background functions with periodicities, such as may result from some amorphous scattering from the sample, Fourier filtration techniques can be used, and other techniques are available for background removal in the presence of discontinuities, such as vanadium absorption edges from sample cans etc.

Providing background subtraction is carried out carefully, in principle there is no reason why neutron powder diffraction data cannot produce thermal parameters of an accuracy approaching those refined from single crystal experiments. It should be borne in mind in practice, however, that negative thermal parameters appearing in a profile refinement do not necessarily imply the refinement is poor, but rather could indicate inadequacies in the background subtraction. In comparison with X-ray studies, thermal parameters are much less critically dependent on absorption corrections.

2.9 MAGNETIC STUDIES

Because neutrons possess a magnetic moment, in addition to scattering from the nuclei of the sample material, they can also scatter from any unpaired or aligned electronic spin present in the sample. The effect of scattering from such ordered spin structures is to produce extra Bragg peaks in the diffraction pattern. Since magnetic scattering takes place from unpaired electrons which normally reside in the valence shell of a particular atom, there is a magnetic form factor fall-off analogous to that of the electronic form factor (scattering factor) for X-rays. This fall-off is due to interference of waves scattered from different electrons in a particular atom (which are wavelength-sized distances apart). This magnetic form factor fall-off is quite severe, and for all but the very smallest $\sin\theta/\lambda$ (longest d-spacing) reflections can be very difficult to detect.

Time-of-flight sources have both disadvantages and advantages for magnetic scattering studies. One disadvantage is the relatively high flux of short wavelength neutrons produced by a t-o-f source. These short λ neutrons are less well suited to the detection of large d-spacing magnetic reflections. However, there is a λ^4 term from the reflectivity of a crystal which to some extent compensates for this. In broad terms the fall off of ISIS intensity seen on HRPD at longer wavelength is of the order of λ^{-5}, and the result is a $1/\lambda$ flux distribution in the region of interest for magnetic studies. One major advantage of pulsed sources is that with reflections at very low 2θ values, detected in a low angle bank, extremely high resolution can still be maintained and so magnetic reflections detected with good accuracy in this geometry.

In several samples studied on HRPD the large d-spacing peaks resulting from magnetic ordering in a material have been seen, and the provision of a 90° and a low angle bank will facilitate future studies of this nature. The adaptation of the profile refinement codes to handle magnetic structures is in progress, as is the general integration of

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these into the CCSL procedures. It is hoped that the capability to perform quantitative magnetic studies will soon be available.

2.10 MULTI-PHASE REFINEMENT

Under circumstances where sample preparation may be particularly
difficult, often the resulting material does not consist purely of a
single phase. There may be several different powder samples which are
inseparable by standard procedures. For these, the resulting diffraction
pattern will be a combination of that from the component crystal
structures, one corresponding to each phase. In the most favourable
situation, the cells corresponding to each system are so disparate as to
make the patterns essentially distinct from each other (i.e. there are
no overlapping peaks from different phases). Under these circumstances
it may be possible to refine each phase independently of the others, by
concentrating attention on just those regions of the pattern
corresponding to the peaks from the phase under examination.

The more usual situation, however, is that the patterns are hopelessly
intermingled, with unresolved peaks containing intensity contributions
from two or more of the component phases, and any attempt to refine a
single phase independently is certain to be unsuccessful. For these
problems a genuine "multi-phase" procedure is required. In such a
procedure, one should have a whole series of crystal data files
containing refinement information for each of the phases present in the
sample, and the refinement program should refine all the parameters for
all the phases, while keeping a check on inter-phase scale factors to
allow for the situation of overlapped contributions from several phases.
In this way, good structural parameters can be obtained for each
component, while keeping the overall calculated profile in good
agreement with that observed.

There is a test multi-phase profile refinement program available at
ISIS, based around the usual framework, and allowing refinement of the
parameters of up to 9 phases simultaneously.

2.11 PEAK SHAPE VARIATIONS - SAPS

Often in a sample there is some effect leading to some variation in the peak shape across the pattern (see e.g. Line Broadening above). This may or may not be (hkl) dependent and so the existing peak shape parameters such as the Gaussian and Lorentzian terms discussed earlier may not be adequate to deal with this.

A general procedure to allow for peak shape variations must therefore include (hkl) dependent and independent capability and in its most general form would involve the capability for "learning" the shape of each individual peak and adjusting the parameters appropriately to deal with this. Such a procedure is in testing and is called SAPS (Structure And Peak Shape) (David, 1988). This allows the profile to be refined using the known structure and the peak shapes to be adjusted as appropriate to improve the fit across the pattern. It is hoped that use of such a procedure will enable the physics contained in subtle peak shape variations to be extracted. The high resolution of diffractometers such as HRPD have allowed this type of study to be contemplated and some unique and previously inaccessible science should be apparent in the peaks given that instrumental broadening is so small.

2.12 SIMULTANEOUS X-RAY AND NEUTRON PROFILE REFINEMENT

A major restructuring of the CCSL based profile refinement routines is in progress which will increase the capability of the procedure. The intention is to have the ability to :

Simultaneously refine X-ray and neutron patterns of the same material;

Extract intensities and refine the unit cell (CAILS) of X-ray and neutron patterns simultaneously;

Profile refine on several phases simultaneously (multi-phase, see above);

Perform CAILS on some phases while profile refining on others;

The capability to simultaneously handle constant wavelength neutron, time-of-flight neutron, X-ray and synchrotron powder diffraction data sets on single or multi-phase data sets;

Etc.

The idea of this new system is to provide a full capability for manipulating structural data from several samples and several sources simultaneously, in order to maximise the information extracted from these data. It is hoped that this will be available soon for users at ISIS.

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NEUTRON POWDER DIFFRACTION DATA ANALYSIS AT ISIS

PRACTICAL ASPECTS

SECTION 5

1 SETTING-UP AND RUNNING A PROFILE REFINEMENT CALCULATION

1.1 PREPARATION OF A NORMALISED DATA FILE

Shown overleaf is a typical command file used for the normalisation of LAD data. The preparation of a normalised data file will normally be performed in the following two ways:

(i) The GENIE workspace containing the final normalised profile should be written out into a file using the GENIE WRITE command. This will enable rapid recall of the desired plot for display purposes (and for any further analysis deemed necessary). The commands required are :

> **WRITE/OPEN Wn RUNxxxx.NOR**   (WR/OP) (OPEN not essential)

> **WRITE/CLOSE**   (WR/CL)

(NB This last command WRITE/CLOSE is essential. If it is omitted the file produced cannot easily be read back into GENIE).

To allow for quick display of this .NOR file, the GENIE READ command is used as follows :

> **READ Wn RUNxxxx.NOR**   (RE)

> **DISPLAY Wn**   (D)

which will result in the contents of RUNxxxx.NOR being displayed on the terminal screen;

(ii) A file should be prepared which contains the profile data, consisting of point-by-point values of the normalised diffraction profile across the pattern. This file will contain the data used by the profile refinement programs. To prepare this file, which conventionally has the extension .DAT, the following commands are required :

> **FUNCTION Wn TF:PROLSFILE Wn**   (FU)

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Enter profile data filename : **MNEMON.DAT**

GENIE command file for the normalisation, by Vanadium of a
Sample Spectrum on LAD

```
!                       LAD NORMALISATION COMMAND FILE
!
> SET DISK LAD$DISK              !! Set pointers to the correct disk
> SET DIR [LADMGR.DATA]          !! directory
> SET INST LAD                   !! and instrument
> SET WORK 10 10000              !! Initialise work arrays
$ INQUIRE ISAM "Give sample run number"
$ INQUIRE IVAN "Give vanadium run number"
> ABB 'ISAM' SA     !! Abbreviate sample data-file to SA for convenience
> ABB 'IVAN' VA     !! Abbreviate V data-file to VA for convenience
> ASS 'ISAM'        !! Assign sample data as default
!! 150 degree bank data are held in spectra 1-8 on LAD
> W1= SA(S1>S8)     !! Fill workspace 1 with sample spectrum
> FU W1 HRPD$DISK:[HRPMGR.LAD]DELAY W1  !! Subtract delayed neutron fraction
> SET PAR W1 10.0  1.129 150 0 1        !! Set parameters for W1
!! Monitor spectrum is held in spectrum 21 on LAD
> W2= SA(S21)       !! Fill workspace 2 with sample monitor spectrum
> SET PAR W2 10.0 -1.095 180 0 1        !! Set parameters for W2
> ASS 'IVAN'        !! Assign vanadium data as default
> W3= VA(S1>S8)     !! Fill workspace 3 with V spectrum
> FU W3 HRPD$DISK:[HRPMGR.LAD]DELAY W3  !! Subtract delayed neutron fraction
> SET PAR W3 10.0  1.129 150 0 1        !! Set parameters for W3
> U/LAM W3          !! Convert V spectrum to wavelength for absorption correction
> FU W3 HRPD$DISK:[HRPMGR.LAD]VANABS W3 !! Correct for absorption in V
> W4= VA(S21)       !! Fill workspace 4 with vanadium monitor spectrum
> SET PAR W4 10.0 -1.095 180 0 1        !! Set parameters for W4
> U/LAM W1          !! Convert sample spectrum to wavelength scale
> U/LAM W2          !! Convert sample monitor spectrum to wavelength scale
> U/LAM W4          !! Convert V spectrum to wavelength scale
> REB W1 W2              !!
> REB W1 W3              !! Make all spectra commensurate
> REB W1 W4              !!
> W5=W3/W4          !! Vanadium / Vanadium monitor
> W6=W1/W2          !! Sample / Sample monitor
> SET PAR W5 10.0  1.129 150 0 1        !! Set parameters for W5
> SET PAR W6 10.0  1.129 150 0 1        !! Set parameters for W6
> SET YCODE W5 -1               !! N.B. W5 is quotient of spectra
> SET YCODE W6 -1               !! N.B. W6 is quotient of spectra
> U/D W5       !! Convert to d spacing scale to simplify V peak removal
> W5=1/W5      !! Invert for ease of fitting
> FU W5 HRPD$DISK:[HRPMGR.LAD]VANPKR W5 !! Remove V peaks
> W5=1/W5      !! "Re-invert" W5
> U/T W5       !! Convert W5 to time-of-flight scale
> U/T W6       !! Convert W5 to time-of-flight scale
> W7=W6/W5     !! Obtain normalised sample spectrum
> D W7         !! Display normalised spectrum
>
!
```

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TITLE : La2SrCu2O8

Raw LAD data for the LASRCU example
(see later)

TITLE : La2SrCu2O8

Normalised LAD data from LASRCU
(see later)
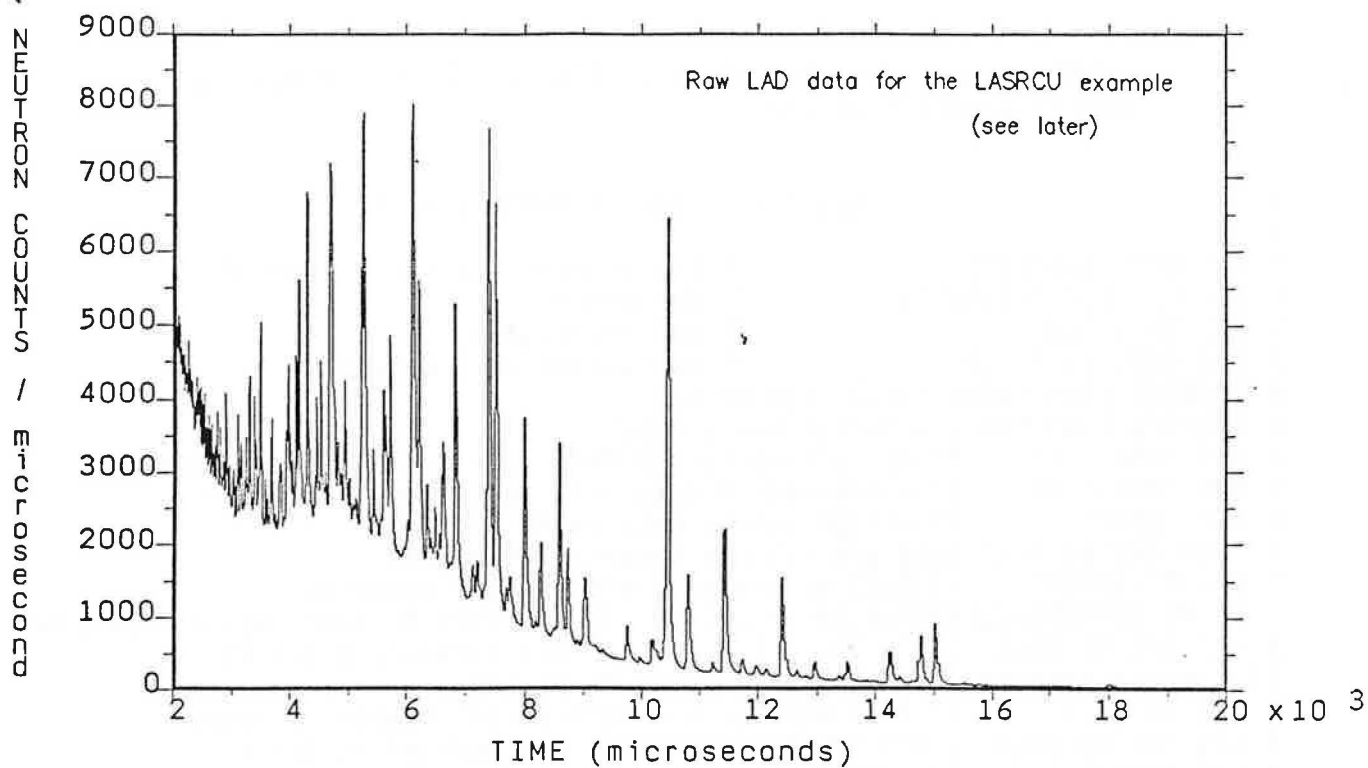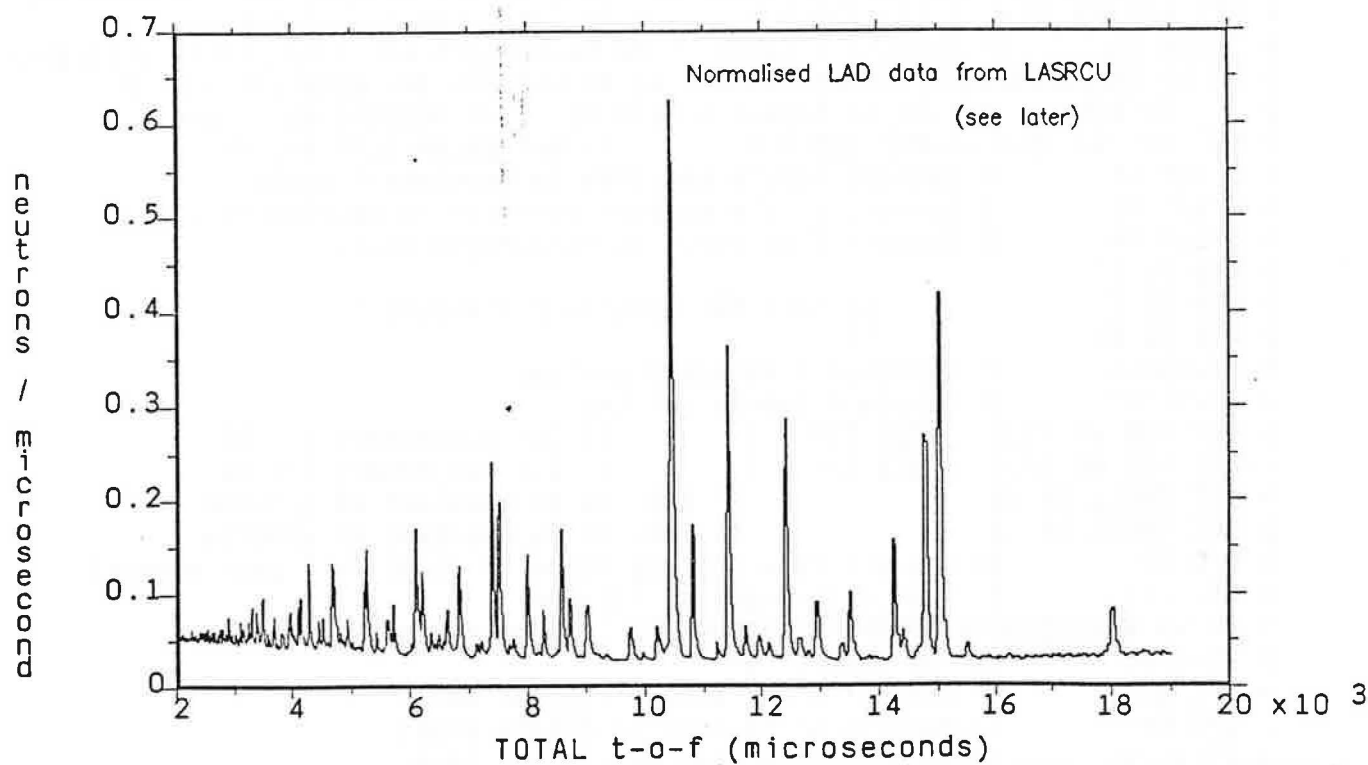
The file name MNEMON should consist of some mnemonic by which the structure will be known throughout the refinement procedure, and is limited to a maximum of 6 characters. For example the file AL2O3.DAT was prepared for an Al_2O_3 refinement, Y123.DAT for a refinement of $YBa_2Cu_3O_{7-x}$.

1.2 PREPARING FOR A REFINEMENT - THE CRYSTAL DATA FILE

The profile refinement codes used to process HRPD data are based around the CCSL routines. There is a technical manual for CCSL available which gives full details of the general use of the library. A quick scan through the CCSL manual will give the user a general feel for the procedure to adopt in using of the library and hence of the profile codes. The instructions documented in this handbook will hopefully be complementary to those in the more specialist CCSL manual, and consequently will go into no great detail regarding technical details of any of the CCSL routines.

One area of overlap will be pursued at length, however, and that is the setting up of a crystal data file. The crystal data file is the means by which the CCSL routines are informed of crystallographic information regarding the sample. In addition this file contains the parameters controlling the course of the refinement as it proceeds and so is fundamental to the whole process.

To prepare a crystal data file, EDIT a file with the name MNEM.CCL, .CCL being the default extension for crystal data files in the CCSL system. Using the full screen editor which has been described earlier, one should input the following lines (cards) into the .CCL file :

N or Title card

N **Title, consisting of up to 80 characters of text**
   (serving to identify the refinement)

   Example
   N Al203 refinement as test example for workshop

C or Cell card

C a   b   c   α   β   γ
   (in Å and °)

   Example

```
C  4.75644  4.75644  12.98793  90  90  120
```

If any of α, β, γ omitted, assumed $= 90°$, except for hexagonal, trigonal cells, where $\gamma = 120°$ is deduced. If either of b, c omitted, assumed equal to a.

A or Atom card

A **name** x   y   z   B   **(label) s.o.f.**

  (atom name, fractional coordinates, isotropic temperature factor (Å^2), optional label and site occupancy)

Example

```
A Al  0.000  0.000  0.35203  0.6  1.0
A 01  0.69358  0.000 0.25000  0.8  1.0
```

If s.o.f. is omitted, the occupancy is assumed equal to 1.

T or Temperature factor card

T **name**   type   B11   B22   B33   B23   B13   B12

  (atom name, type of anisotropic temperature factor, B_{ij} values (Å^2))

Example

```
T Al  2  0.1027  0.1027  0.25794  0.00  0.00  0.05135
T 01  2  0.14677  0.18811  0.22677  0.03729  0.01866  0.09047
```

The "type" 0 creates an anisotropic temperature factor from an existing isotropic B (i.e. $B_{ij} = B_{iso}$ (i=j), $B_{ij} = 0$ (i≠j), i,j=1,2,3). The temperature factor created is of the type 2 (CCSL manual) :

$$\text{EXP}(-1/4(B_{11} \, ha^*ha^* + \ldots + 2 B_{23} \, kb^*lc^* + \ldots).$$

F or Form factor card

F **name**   type   b

  (atom name, type of scattering factor, scattering length)

Example
```
F Al   1   0.3446
F O    1   0.5805
```

For neutron data, type 1 is for a neutron scattering length.

S or Symmetry cards

S $s_x(x)$, $s_y(y)$, $s_z(z)$
    (symmetry operators defining the space group)

Example
```
S   1/3+X, 2/3+Y, 2/3+Z
S   -X, -Y, -Z
S   Y, X, 1/2-Z
S   -Y, X-Y, Z
```

Only the unique generators as defined in the International Tables for Crystallography Vol. A are required.

The above cards have defined the crystal cell, symmetry and contents. In this sense the "crystal data" file is complete. However, for profile refinement this file contains further cards which guide the course of the refinement procedure.

I or Information cards

This card controls much of the output of data. For full definition of possible parameters see the CCSL manual.

Example
```
I NCYC 5 MCOR 0 PRIN 0 PRFO 0 PRPR 2 PRFC 0 BMIN 0.8 BMAX 2.4
```

In the above example, the I card informs the program :

NCYC 5 - 5 cycles of least squares refinement
(NCYC 0 - Simulation required)

```
MCOR 0 - Print out whole correlation matrix
PRIN 0 - Do not print output data lists
PRFO 0 - Do not print Fourier file
PRPR 2 - Output reflection listing on first and last cycles
PRFC 0 - Do not print Observed and Calculated integrated intensities
BMIN 0.8 - Prepare bond scan with minimum bond length of 0.8Å
BMAX 2.4 - Prepare bond scan with maximum bond length of 2.4Å
```

L or Least squares cards

These cards are used both to provide parameters information to the refinement and also to control the variation of parameters, and hence can be split into two types.

Examples of Parameter L cards

L REFI -11

Card defining the type of refinement (+/-11 for profile, +11 includes refinement of background between reflection positions, -11 excludes these)

L RTYP 2 50000. 100000.

Card defining data range (3 for generate then delete reflections, 2 for generate and append reflections, 1 for reflections available and appended to .CCL file, minimum time of flight 50000 µs, maximum t-o-f 100000 µs in this case)

L WGHT 3

Weighting to be used in refinement (3 for $1/\sigma^2$)

L THE2 168.329

Average 2θ value of detectors (fixed by instrument geometry (168.329° for HRPD 1m position))

L ZERO 8.00

Zero-point correction (in µs)

L PKCN 96.0505 0.000

Peak centre (in m, the first parameter is fixed by the instrument geometry (96.0505m for HRPD 1m position))

L SCAL 1.00

Scale factor

L BACK 0.65432 -0.21456 0.03197 0.00218 0.00045

    Background parameters - a polynomial fit is performed and refined to account for the general background in the pattern. Usually 5 parameters are sufficient.

L PKFN SWCH

    Peak shape switch function

L PKFN TAUF

    Peak shape fast exponential decay

L PKFN TAUS

    Peak shape slow exponential decay

L PKFN SIGM

    Peak shape Gaussian component width

L PKFN GAMM

    Peak shape Lorentzian component width

L EXTN 1 4.5

    Extinction correction (1 represents type of model, in this case Gaussian, along with domain size in microns)

L PROR 1 0.9 1 -1 1

    Preferred orientation correction (1 represents type of model, 0.9 is r, the March coefficient, followed by (H K L) of the preferred orientation direction.

Examples of Control L cards

L VARY ONLY SCAL 1 BACK 1 BACK 2 BACK 3 BACK 4 BACK 5

    If ONLY keyword is omitted, a set of default parameters are refined, including atomic coordinates and unit cell. This card restricts the refinement to only those quoted on this and later L VARY cards. Typically this card varying scale and background would be the first issued in a refinement procedure.

L VARY ZERO 1 PKCN 2

    Varying zero-point and peak centre parameters

L VARY A* B* C*

    Varying cell dimensions, the parameters refined are related to the reciprocal cell dimensions $A^*=a^{*2}$, $B^*=b^{*2}$, $C^*=c^{*2}$ ...

L VARY D* E* F*

... $D^* = 2b^*c^*\cos\alpha^*$, $E^* = 2c^*a^*\cos\beta^*$, $F^* = 2a^*b^*\cos\gamma^*$.

L VARY ALL XYZ

    Vary all atomic coordinates

L VARY O1 X

    Vary the x coordinate of atom O1

L VARY ALL BIJ

    Vary all anisotropic temperature factors

L VARY Al B11 O1 ITF

    Vary B_{11} of atom Al and isotropic temp. factor for atom O1

L VARY Al SITE

    Vary site occupancy of atom Al

L VARY SIGM 2 SIGM 3

    Vary Gaussian width parameters of the peak shape

L FIX CARDS

    See examples

L RELA CARDS

    See examples

1.3 GENERAL PROFILE REFINEMENT STRATEGY

The data having been collected, focused, normalised and the normalised files written as .DAT files, one proceeds to refinement.

The first parameters refined, as discussed above, should be the background and scale. Remember to include the keyword ONLY on the first L VARY card issued, otherwise the refinement will be overambitious in its early stages and may not converge. Since the refinement of scale and background involve only coefficients of ordinary or orthogonal polynomials the problem is linear and should converge immediately (after 1 cycle) from whatever starting parameters are provided.

Card : L VARY ONLY SCAL 1 BACK 1 BACK 2 BACK 3 BACK 4 BACK 5

The next step is to accurately locate the Bragg peaks by means of refining the cell dimensions and possibly the zero-point parameter. Initially reasonable estimates of cell dimensions are required for this stage in the refinement.

Card : L VARY A* B* C*

Then possibly (although PKCN 2 should not be needed)

Card : L VARY ZERO 1 PKCN 2

Atomic parameters should then be varied. Firstly the positional parameters of all atoms are released, which will alter the peak areas to improve the fit. Once these have stabilised, temperature factors are refined to account for atomic vibrations. If the data are of sufficient quality it may be possible to refine all B_{ij} parameters anisotropically, but only if this leads to a reliable and significant improvement over an isotropic description of the harmonic displacements of the atoms.

Card : L VARY ALL ITF
       L VARY ALL BIJ

Assuming that the refinement to date has proceeded satisfactorily, one can vary the peak shape parameters across the pattern to take account of sample broadening effects. Both Gaussian and Lorentzian components of this are available to be refined from HRPD data, and with the very high resolution of the instrument, frequently these parameters are very significant factors in the profile and hence in the least squares procedure.

Card : L VARY SIGM 2 SIGM 3
       L VARY GAMM 2 GAMM 3

1.4 RUNNING THE PROFILE REFINEMENT CALCULATION

Once one has logged in to either the HUB (VAX 8650) or to the HRPD FEM (μ-VAX-II) as an HRPD user, as described elsewhere, there are set up a wide range of abbreviated commands to make performing a profile refinement as straightforward as possible. In the following, we assume that the normalised data file MNEMON.DAT is available and that a MNEMON.CCL file has been set up in the user's area.

There are two ways in which the PR calculation can be run :

1. By explicitly running the program and answering the prompts with the appropriate filenames. This procedure is useful if one wishes to use non-standard filenames for some reason.

2. By implementing the appropriate command procedure, using the abbreviation set up for this purpose. This is the normal way of proceeding.

1.4.1 Running the profile refinement program explicitly

The command required to do this is

    $ RUN [HRPMGR.CCSL.EXE]PROGRAM

to which the program will prompt as follows :

Give name for Output file   **MNEMON.OUT**
Give name of Crystal data file   **MNEMON.CCL**
Give name for New Crystal Data file   **MNEMON.CCN**
Give name of Observations file   **MNEMON.DAT**

The program will now commence execution, writing lineprinter output to the file MNEMON.OUT. Typically the output to the screen will look as follows :

```
>>> commencing cycle    1
Chi squared =   10.7587 for    768 observations and  10 basic variables
>>> commencing cycle    2
Chi squared =    6.3598 for    768 observations and  10 basic variables
>>> commencing cycle    3
Chi squared =    5.6180 for    768 observations and  10 basic variables
>>> commencing cycle    4
Chi squared =    5.5429 for    768 observations and  10 basic variables
>>> commencing cycle    5
```

This example is one with 5 least squares cycles, and before commencing the final cycle, a filename is requested for output of the data required for plotting of the profile and fit :

```
Give name for File to output Profiles   MNEMON.PRO
```

and the program continues :

```
Chi squared =    5.5416 for    768 observations and  10 basic variables
FORTRAN STOP
```

The modified crystal data corresponding to the refined values are written out to the file MNEMON.CCN (for New).

1.4.2 The command procedure approach
To perform the same calculation using the command procedure one would issue the command

    $ **PROGRAM MNEMON (QUEUE)**

where the abbreviation PROGRAM is set up to run the command procedure [HRPMGR.WORKSHOP.COMMAND]PROGRAM.COM and will use the filenames given

explicitly in the example above (MNEMON.OUT, .CCL, .CCN, .DAT, .PRO) automatically. The optional parameter QUEUE should be used to submit jobs to the batch queues FAST (CPU < 1 minute), BATCH (CPU < 15 minutes) or SLOW (unlimited CPU).

If run interactively, the command procedure will produce identical screen output to the example above, and in batch the same information os written off to the .LOG file. When a batch job is implemented it will be named BATCH_TF_MNEMON and the log file will be in the top level directory of the user area and will be called [DEMOxx]TF_MNEMON.LOG.

1.4.3 Examining the profile fit

Having performed the refinement, one is obviously interested in looking at the profile fit to examine the quality of this at this stage. The GENIE program is used to do this. Once again, things are set up to make this procedure as straightforward as possible.

Begin the GENIE session

$ **GENIE**

and once the GENIE prompt (>>) is obtained, issue the following command to begin a profile plot :

>> **PS**   PS (Profile Start) runs the command procedure
                   [HRPMGR.GENIE.PUBLIC]PS

The procedure will prompt as follows :

```
>>
>>
>>   *** Powder profile plotting routine ***
>>   *** no background will be displayed ***
>>
>> T M
```

```
         point plotting mode selected
>> A M 1
>> T H
      no graph header will be displayed
>> A P 0 1 0 0.8
>>    Data file name (no extension) please? :  MNEMON
>> LO W1 MNEMON.PRO G:PROF_OBS
   loading observed data points
   ...
>> LO W2 MNEMON.PRO G:PROF_CALC
   ...
>> LO W3 MNEMON.PRO G:PROF_DIFF
   ...
>>
>>   Lower and upper limits? :  80000 125000
>>   Group into N bins. Give N :  3
>>
>> A B 3
>> D/M W1 80000 125000
```

At this point the plot of the observed profile will appear (as points).
<CR> should be hit once the plot has finished, to allow the calculated
profile to be plotted.

```
>> P/L W2 1
```

At this point the plot of the calculated profile will appear (as a
line). <CR> ends the plotting.
If the OBS and CALC profiles show reasonable agreement, one may wish to
look at a difference plot. The GENIE workspace W3 contains this
information and can be plotted onto the pattern. For convenience and
clarity, it is usual to add to W3 some value in order to place the
difference plot at the top of the profile plot. A sensible value to add
can be seen from the existing plot. Assuming that dispacing W3 by 18
along the Y axis would lead to a sensible placing of the difference

plot, the commands

>> W3=W3+18
>> P/L W3

will lead to the display of the difference plot on the same graph as the OBS and CALC profile plots. If a laser plot of this is required, issuing the command

>> HC   HC (Hard Copy) executes the command procedure
                 [HRPMGR.GENIE.PUBLIC]HC
>> HC1   HC1.....HC1
>> HC2   HC2.....HC2

at this point will give this (the plot will emerge on the laser printer on the first floor of R3 (HC), or the second floor (HC1) or in the DAC (HC2)).

If one requires to look at a different range of the data in the profile file which has already been loaded by use of PS, one can use the procedure PC (Profile Continue) which is less time consuming as it uses the already existing GENIE workspaces.

>> PC   @[HRPMGR.GENIE.PUBLIC]PC

to which the command procedure responds

>> Lower and Upper limits? : 50000 80000
>> Group into N bins. Give N : 5
>>
>> A B 5
>>
>> D/M W1 50000 80000
          (User : <CR>)
>> P/L W2 1
          (User : <CR>)

Once again a difference plot can be added, but it should be borne in mind that W3 may already have had a Y shift added if an earlier difference plot has been carried out. A suitable modification to this shift may be required to allow W3 to adopt a sensible position in the new (continued) plot.

1.4.4 Continuing a refinement

Assuming that the refinement to date looks promising, and that the profile fit looks not unreasonable, then one obviously would wish to continue the refinement, perhaps to vary more parameters etc. The procedure to follow to do this is straightforward. Since the updated crystal data file information is held in the file MNEMON.CCN, one simply edits this file to include any new information required for the next refinement, and renames the modified file to be MNEMON.CCL, in order that this is used as the crystal data input. The simplest way to do this is by using the command

```
$ EDIT MNEMON.CCN /OUT=MNEMON.CCL
```

which automatically renames the output file when one EXITs from the EDT editor.

The new MNEMON.CCL file can then be used as input to the refinement and the above procedure repeated.

A flow diagram of the basic refinement procedure is given in the Figure below and a more complicated one overleaf.

```
COLLECT DATA ──────────┐
                       │
              NORMALISE DATA
                       │
        CREATE .CCL FILE
                       │
    EXECUTE PROFILE REFINEMENT
                       │
    DISPLAY PROFILE USING GENIE
                       │
    EDIT .CCN FILE TO VARY DIFFERENT
    PARAMETERS ──> NEW .CCL FILE
```
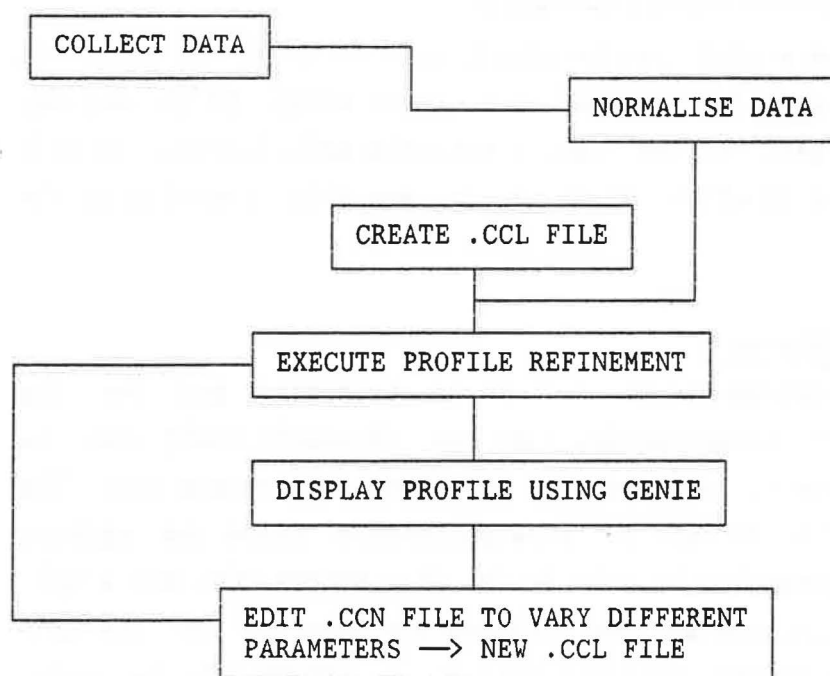
Figure - Flow diagram of the profile refinement procedure.

Also shown overleaf is a commented AL203.CCL file for refinement of AL203 data from LAD.

CCSL PROFILE REFINEMENT FLOW DIAGRAM

```
┌─────────────────────────────────────────┐
│      INITIALISE CRYSTALLOGRAPHIC DATA    │
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│       INITIALISE LEAST SQUARES PROBLEM   │
│            SET UP VARIABLE NAMES         │
│        DETERMINE WHICH PARAMETERS TO     │
│     VARY, FIX OR RELATE TO ONE ANOTHER   │
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│      READ IN / GENERATE REFLECTION INDICES│
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│   READ IN OBSERVED DATA i.e. XOBS YOBS EOBS│
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│  CALCULATE MIN AND MAX CONTRIBUTING REFLECTIONS,│
│  KMIN(I) AND KMAX(I) FOR EACH OBSERVATION I  &  │
│  FILE XOBS(I),YOBS(I),EOBS(I),KMIN(I),KMAX(I)   │
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│        START CYCLE OF REFINEMENT         │
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│          INITIALISE R FACTOR SUMS        │
│          AND LEAST SQUARES MATRIX        │
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│       READ IN OBSERVATION NUMBER I       │
│   XOBS(I),YOBS(I),EOBS(I),KMIN(I),KMAX(I)│
└─────────────────────────────────────────┘
     NO ─┤   EXCLUDE THIS POINT ?   ├─ YES
     NO ─┤ REFLECTION AT THIS POINT ? ├─ YES
┌─────────────────────────────────────────┐
│     CALCULATE PEAK FUNCTION & DERIVATIVES│
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│        CALCULATE BACKGROUND VALUE        │
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│    EVALUATE YCALC(I)= YPEAK(I)+YBACK(I)  │
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│   CALCULATE USEFUL STATISTICAL QUANTITIES│
│   FOR OBSERVATION I AND ADD INTO R-FACTORS│
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│       ADD DERIVATIVES INTO LSQ MATRIX    │
└─────────────────────────────────────────┘
     NO ─┤   ANY MORE OBSERVATIONS  ?   ├─ YES
┌─────────────────────────────────────────┐
│   IF PRESENT CALCULATE SLACK CONSTRAINTS │
│   (TREATED AS EXTRA OBSERVATIONS)        │
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│             PRINT R FACTORS              │
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│            INVERT LSQ MATRIX             │
│   CALCULATE PARAMETER SHIFTS AND ESDs    │
│  APPLY NEW SHIFTS : PRINT OUT VARIABLES  │
└─────────────────────────────────────────┘
     NO ─┤   PENULTIMATE CYCLE ?   ├─ YES
     NO ─┤ LAST CYCLE ├─ YES
┌─────────────────────────────────────────┐
│        PRINT NEW CONTROL FILE            │
│        OBS /CALC OUTPUT FILE             │
│        FOURIER DATA FILE                 │
└─────────────────────────────────────────┘
┌─────────────────────────────────────────┐
│       PRINT CORRELATION MATRIX           │
└─────────────────────────────────────────┘
┌─────────┐
│   END   │
└─────────┘
```

Cambridge Crystallography Subroutine Library Control File
for TOF Profile Refinement of Al2O3 data on LAD

```
N   Al2O3 -- Standard sample on LAD -- users AKS / WSH.
Z.. This data set was normalised to a vanadium spectrum using
Z.. [HRPMGR.LAD]LADNORM.COM on 3-OCT-1987 by WIFD / CCW.
Z.. i.e. Al2O3(#172)/Vanadium(#171)
Z
Z.. Information (I) card principally controlling output of data
I NCYC 5 MCOR 0 PRIN 0 PRFO 0 PRPR 2 PRFC 0 BMIN 0.0 BMAX 2.4
Z.. Bond length / angle (B) card : used in bond length / angle calculation
Z.. but not used in profile refinement code.
B BOND
Z.. Cell (C) cards
C   4.75644   4.75644  12.98793   90.000   90.000   120.000
Z.. Atom (A), anisotropic temperature factor (T) and form factor (F) cards.
Z.Name       x         y         z         B           occupancy
A Al     0.00000   0.00000   0.35203   0.00000
A Ox     0.69358   0.00000   0.25000   0.00000
Z.Name  type    B11       B22       B33       B23       B13       B12
T Al     2    0.10270   0.10270   0.25794   0.00000   0.00000   0.05135
T Ox     2    0.14677   0.18811   0.22677   0.03729   0.01866   0.09407
F Al     1    0.34460
F Ox     1    0.58050
Z.. Symmetry (S) cards - space group generator symmetry elements only required.
S   1/3+X,2/3+Y,2/3+Z
S  -X,-Y,-Z
S   Y,X,1/2-Z
S  -Y,X-Y,Z
Z.. Least squares (L) cards:
Z.. These cards give the type of least squares, the profile parameters and
Z.. which parameters are to be varied.
L REFI -11
Z..              tmin     tmax
L RTYP   2      2000.    15000.
L WGHT 3
Z.. Scale factor and background cards:
Z.. Background type 2: Shifted Chebyshev (1st kind) orthogonal polynomials.
L SCAL   0.32050
L BACK   2       0.33801   -0.33525   0.11850   -0.01473   0.05820
Z.. Zero point (microseconds), peak centre (d spacing to TOF) and 2 theta card.
L ZERO   3.6403
L PKCN  11.0700   -0.4974
L THE2 150.000
Z.. Peak shape descriptor cards:
L PKFN TAUF   8.0000    0.0000    4.1658
L PKFN TAUS   8.0000   31.0272    1.4031
L PKFN SIGM   5.0000    2.5486   13.4975    0.0000
L PKFN SWCH   1.0000    4.5833    0.6638
Z.. Extinction correction card:
L EXTN   1    4.4977
Z.. The remaining cards control which parameters are to be varied.
Z.. Also possible are L FIX and L RELA cards. Symmetry-related parameters
Z.. are automatically related to one another. (e.g. for Al, B11 = B22 = 2B12)
Z.. In general, the peak shape parameters associated with instrumental
Z.. contributions are fixed; only those associated with sample broadening
Z.. should be varied. In the present example these are SIGM 1 and SIGM 2.
L VARY ONLY SCAL 1 BACK 1 BACK 2 BACK 3 BACK 4 BACK 5
L VARY ZERO 1 A* C* PKCN 2
L VARY ALL XYZ ALL BIJ
L VARY EXTN
L VARY SIGM 1 SIGM 2
```

2 A PROFILE REFINEMENT EXAMPLE

2.1 A BASIC PROFILE REFINEMENT - LASRCU $(La_2SrCu_2O_6)$

2.1.1 The starting .CCL file - varying scale and background

For the refinement of the high-T_c superconductor-related material $(La,Sr)_2Cu_2O_6$ (LAD data) used as an example in this workshop, the first LASRCU.CCL to be created took the following form :

```
N La2SrCu206 LAD run 902 I4/mmm (139)
Z Approximate cell input
C    3.86    3.86   19.96     90.000    90.000    90.000
Z Symmetry operators
S -X,-Y,Z
S -Y,X,Z
S -X,Y,-Z
S -X,-Y,-Z
S 1/2+X,1/2+Y,1/2+Z
Z initial La1/Sr1 50:50     La2/Sr2 75:25
Z Atoms
A La1     0.00000     0.00000     0.00000     0.5         0.5
A Sr1     0.00000     0.00000     0.00000     0.5         0.5
A La2     0.00000     0.00000     0.17859     0.3         0.75
A Sr2     0.00000     0.00000     0.17859     0.3         0.25
A Cu      0.00000     0.00000     0.59306     0.3
A 01      0.00000     0.50000     0.08589     0.5
A 02      0.00000     0.00000     0.70125     1.3
Z Note the guessed thermal parameters (set to "reasonable" values)
Z Form factors (scattering lengths)
F La        1    0.82700
F Sr        1    0.70200
F Cu        1    0.77180
F O         1    0.58050
Z Preparation for a bond length output (if required)
B BOND
Z Controlling the run and output
I NCYC 3 MCOR 0 PRIN 0 PRFO 0 PRPR 2 PRFC 0 BMIN 0.0 BMAX 3.0
Z Beginning L cards
L REFI -11
L RTYP     2  2000.0 19000.00
L BACK     2  0 0 0 0 0
L WGHT 3
L THE2 150.000
L SCAL     1.00
L ZERO     8.00
L PKCN    11.0700      0.0000
L PKFN TAUF    8.0000      0.0000      2.3500
L PKFN TAUS    8.0000     32.0000      0.0000
```

```
L PKFN SIGM    4.0000    0.0000   10.0000    0.0000
L PKFN SWCH    1.0000    3.5136    0.6787
Z Varying just scale and background
L   VARY  ONLY  SCAL   1 BACK  1   BACK  2  BACK   3 BACK  4   BACK  5
```
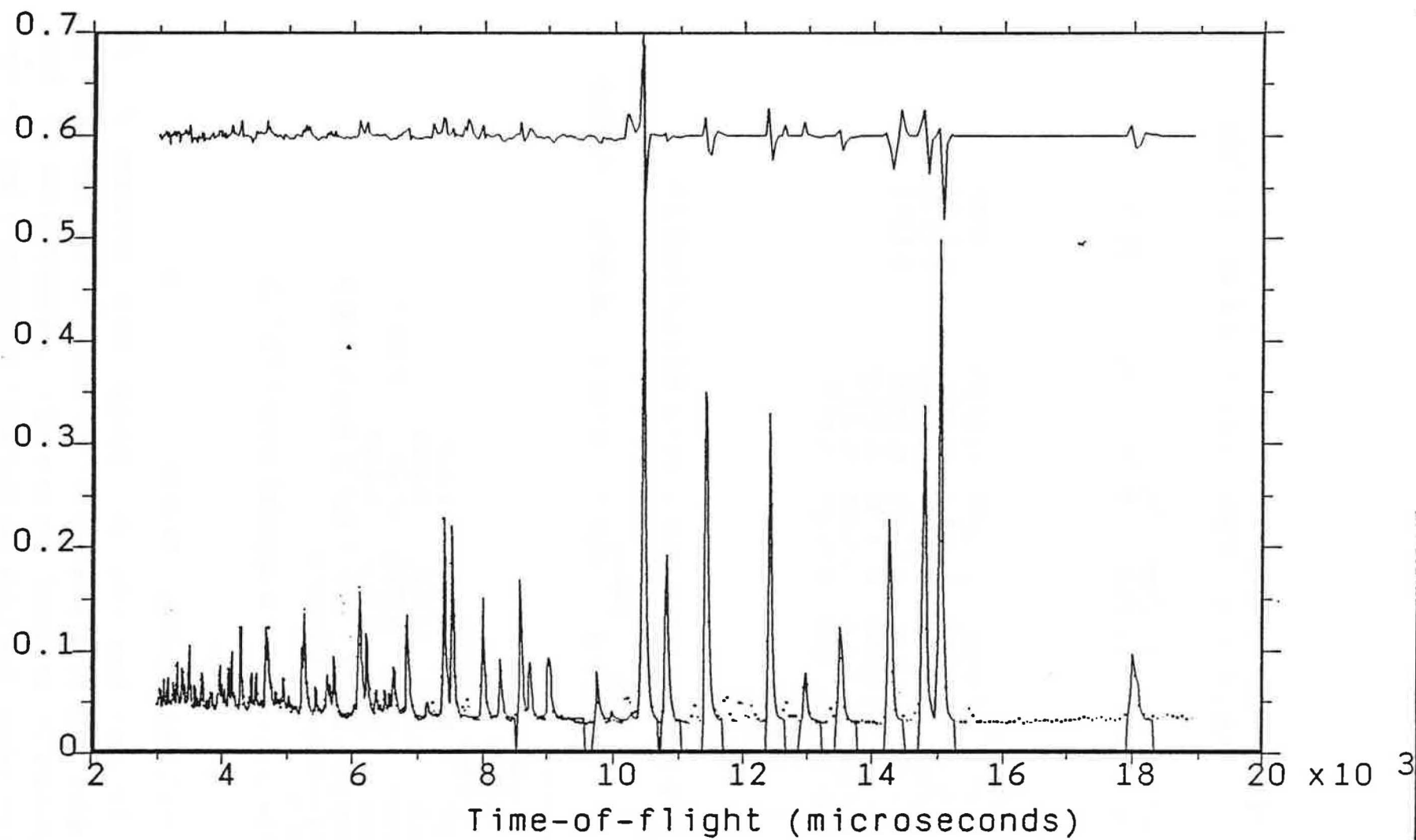
The χ^2 from this refinement went as follows through the 3 cycles :

     *** (>10000) → 59.4980 → 59.4903 ,

and the profile fitted is shown in the Figure overleaf.

2.1.2 Varying the cell parameters

The LASRCU.CCN produced is now renamed LASRCU.CCL and is shown below :

```
N La2SrCu206 LAD run 902 I4/mmm (139)
C   3.86000    3.86000   19.96000    90.000     90.000     90.000
S -X,-Y,Z
S -Y,X,Z
S -X,Y,-Z
S -X,-Y,-Z
S 1/2+X,1/2+Y,1/2+Z
A La1     0.00000    0.00000    0.00000    0.50000         0.50000
A Sr1     0.00000    0.00000    0.00000    0.50000         0.50000
A La2     0.00000    0.00000    0.17859    0.30000         0.75000
A Sr2     0.00000    0.00000    0.17859    0.30000         0.25000
A Cu      0.00000    0.00000    0.59306    0.30000
A 01      0.00000    0.50000    0.08589    0.50000
A 02      0.00000    0.00000    0.70125    1.30000
F La      1    0.82700
F Sr      1    0.70200
F Cu      1    0.77180
F 0       1    0.58050
B BOND
I NCYC 4 MCOR 0 PRIN 0 PRFO 0 PRPR 2 PRFC 0 BMIN 0.0 BMAX 3.0
L REFI -11
L RTYP    1       2000.      19000.
L BACK    2         0.03658   -0.00731     0.00375   -0.00056     0.00014
L WGHT 3
L THE2 150.000
L SCAL    0.00328
L ZERO    8.0000
L PKCN   11.0700      0.0000
L PKFN TAUF    8.0000     0.0000     2.3500
L PKFN TAUS    8.0000    32.0000     0.0000
L PKFN SIGM    4.0000     0.0000    10.0000     0.0000
L PKFN SWCH    1.0000     3.5136     0.6787
L VARY ONLY SCAL 1 BACK 1 BACK 2 BACK 3 BACK 4 BACK 5
Z Add cell dimension refinement
L VARY A* C*
Z The reflection list is now appended (Note L RTYP 1)
*
   10    0   16    etc.
```

χ^2 : *** → 49.2983 → 39.4786 → 39.4602

As can be seen from this the initial cycle increases the χ^2 considerably. This is an artefact of the initialisation, especially if the parameters to be varied are initially considerably removed from their correc values. Providing the refinement subsequently improves this is nothing to worry about.

2.1.3 Varying atomic coordinates

We continue with another LASRCU.CCN

```
N La2SrCu206 LAD run 902 I4/mmm (139)
C    3.85806    3.85806   19.95439      90.000      90.000      90.000
S -X,-Y,Z
S -Y,X,Z
S -X,Y,-Z
S -X,-Y,-Z
S 1/2+X,1/2+Y,1/2+Z
A La1    0.00000    0.00000    0.00000    0.50000      0.50000
A Sr1    0.00000    0.00000    0.00000    0.50000      0.50000
A La2    0.00000    0.00000    0.17859    0.30000      0.75000
A Sr2    0.00000    0.00000    0.17859    0.30000      0.25000
A Cu     0.00000    0.00000    0.59306    0.30000
A O1     0.00000    0.50000    0.08589    0.50000
A O2     0.00000    0.00000    0.70125    1.30000
F La      1    0.82700
F Sr      1    0.70200
F Cu      1    0.77180
F O       1    0.58050
B BOND
I NCYC 4 MCOR 0 PRIN 0 PRFO 0 PRPR 2 PRFC 0 BMIN 0.0 BMAX 3.0
L REFI  -11
L RTYP     1       2000.          0.
L BACK     2        0.05232     0.00424     0.00017     0.00000     0.00000
L WGHT 3
L THE2 150.000
L SCAL    0.00336
L ZERO    8.0000
L PKCN   11.0700      0.0000
L PKFN TAUF    8.0000      0.0000      2.3500
L PKFN TAUS    8.0000     32.0000      0.0000
L PKFN SIGM    4.0000      0.0000     10.0000      0.0000
L PKFN SWCH    1.0000      3.5136      0.6787
Z This L RELA cards are required since the atoms La1 and Sr1 occupy the
Z same site (and hence the same Z coordinates)
L RELA 1 1.0 La1 Z 1.0 Sr1 Z
Z Ditto for La2 and Sr2
L RELA 1 1.0 La2 Z 1.0 Sr2 Z
L VARY ONLY SCAL 1 BACK 1 BACK 2 BACK 3 BACK 4 BACK 5
L VARY A* C*
Z Vary Zero-point parameter
L VARY ZERO 1
Z Very atomic coordinates (any special positions will not be refined)
L VARY ALL XYZ
* ... and reflections ...
```

χ^2 : 95.1015 $\rightarrow$ 39.1446 $\rightarrow$ 39.1536 $\rightarrow$ 39.1480

It should be noted that if the Z coordinate shifts of La1, Sr1 and La2,

Sr2 are not related by an L RELA command, the refinement is likely to be unstable, since the physical model is then unreasonable.

2.1.4 Gaussian width parameter

Another LASRCU.CCN

```
N La2SrCu206 LAD run 902 I4/mmm (139)
C   3.85856   3.85856   19.95643      90.000      90.000      90.000
S -X,-Y,Z
S -Y,X,Z
S -X,Y,-Z
S -X,-Y,-Z
S 1/2+X,1/2+Y,1/2+Z
A La1      0.00000    0.00000    0.00000    0.50000         0.50000
A Sr1      0.00000    0.00000    0.00000    0.50000         0.50000
A La2      0.00000    0.00000    0.17862    0.30000         0.75000
A Sr2      0.00000    0.00000    0.17862    0.30000         0.25000
A Cu       0.00000    0.00000    0.59308    0.30000
A O1       0.00000    0.50000    0.08614    0.50000
A O2       0.00000    0.00000    0.70182    1.30000
F La       1    0.82700
F Sr       1    0.70200
F Cu       1    0.77180
F O        1    0.58050
B BOND
I NCYC 4 MCOR 0 PRIN 0 PRFO 0 PRPR 2 PRFC 0 BMIN 0.0 BMAX 3.0
L REFI -11
L RTYP    1      2000.          0.
L BACK    2        0.05225    0.00418    0.00016    0.00000    0.00000
L WGHT 3
L THE2 150.000
L SCAL    0.00336
L ZERO    7.1933
L PKCN   11.0700      0.0000
L PKFN TAUF    8.0000     0.0000     2.3500
L PKFN TAUS    8.0000    32.0000     0.0000
L PKFN SIGM    4.0000     0.0000    10.0000     0.0000
L PKFN SWCH    1.0000     3.5136     0.6787
L RELA 1 1.0 La1 Z 1.0 Sr1 Z
L RELA 1 1.0 La2 Z 1.0 Sr2 Z
L VARY ONLY SCAL 1 BACK 1 BACK 2 BACK 3 BACK 4 BACK 5
L VARY A* C*
L VARY ZERO 1
L VARY ALL XYZ
Z Inclusion of Gaussian width as a parameter
L VARY SIGM 2
* ... and reflections ...
```

χ^2 : 81.1596 → 36.9436 → 36.8699 → 36.8510

2.1.5 Thermal parameter refinement

And again a new LASRCU.CCN (with experience some of these iterations can be removed, and more parameters introduced simultaneously).

```
N La2SrCu206 LAD run 902 I4/mmm (139)
C    3.85871    3.85871  19.95828     90.000     90.000     90.000
S -X,-Y,Z
S -Y,X,Z
S -X,Y,-Z
S -X,-Y,-Z
S 1/2+X,1/2+Y,1/2+Z
A La1    0.00000    0.00000    0.00000    0.50000         0.50000
A Sr1    0.00000    0.00000    0.00000    0.50000         0.50000
A La2    0.00000    0.00000    0.17856    0.30000         0.75000
A Sr2    0.00000    0.00000    0.17856    0.30000         0.25000
A Cu     0.00000    0.00000    0.59302    0.30000
A 01     0.00000    0.50000    0.08616    0.50000
A 02     0.00000    0.00000    0.70174    1.30000
F La      1    0.82700
F Sr      1    0.70200
F Cu      1    0.77180
F O       1    0.58050
B BOND
I NCYC 4 MCOR 0 PRIN 0 PRFO 0 PRPR 2 PRFC 0 BMIN 0.0 BMAX 3.0
L REFI  -11
L RTYP    1        2000.          0.
L BACK    2         0.05258    0.00459    0.00021    0.00001    0.00000
L WGHT 3
L THE2 150.000
L SCAL   0.00340
L ZERO   7.0534
L PKCN  11.0700      0.0000
L PKFN TAUF    8.0000      0.0000     2.3500
L PKFN TAUS    8.0000     32.0000     0.0000
L PKFN SIGM    4.0000      0.0000    13.1930      0.0000
L PKFN SWCH    1.0000      3.5136     0.6787
L RELA 1 1.0 La1 Z 1.0 Sr1 Z
L RELA 1 1.0 La2 Z 1.0 Sr2 Z
Z As for Z coords, tie together the appropriate thermal parameters
L RELA 1 1.0 La1 ITF 1.0 Sr1 ITF
L RELA 1 1.0 La2 ITF 1.0 Sr2 ITF
L VARY ONLY SCAL 1 BACK 1 BACK 2 BACK 3 BACK 4 BACK 5
L VARY A* C*
L VARY ZERO 1
L VARY ALL XYZ
L VARY SIGM 2
Z Vary all isotropic temperature factors
L VARY ALL ITF
* ... and reflections ...
```

χ^2 : 325.7825 → 36.1897 → 36.0558 → 36.0336

2.1.6 Site occupancy refinement

Now that we appear to have a reasonably stable refinement, we vary the parameters which are of most chemical interest in this sample, the site occupancies of the La,Sr sites, tying these together as appropriate by L RELA commands

```
N La2SrCu206 LAD run 902 I4/mmm (139)
C   3.85865    3.85865   19.95800      90.000      90.000      90.000
S -X,-Y,Z
S -Y,X,Z
S -X,Y,-Z
S -X,-Y,-Z
S 1/2+X,1/2+Y,1/2+Z
A La1      0.00000    0.00000    0.00000    0.29692      0.50000
A Sr1      0.00000    0.00000    0.00000    0.29692      0.50000
A La2      0.00000    0.00000    0.17862    0.44830      0.75000
A Sr2      0.00000    0.00000    0.17862    0.44830      0.25000
A Cu       0.00000    0.00000    0.59302    0.32203
A 01       0.00000    0.50000    0.08604    0.59541
A 02       0.00000    0.00000    0.70164    1.36769
F La       1    0.82700
F Sr       1    0.70200
F Cu       1    0.77180
F O        1    0.58050
B BOND
I NCYC 4 MCOR 0 PRIN 0 PRFO 0 PRPR 2 PRFC 0 BMIN 0.0 BMAX 3.0
L REFI -11
L RTYP    1       2000.          0.
L BACK    2        0.05381    0.00498    0.00023    0.00001    0.00000
L WGHT 3
L THE2 150.000
L SCAL   0.00346
L ZERO   7.1151
L PKCN   11.0700    0.0000
L PKFN TAUF    8.0000    0.0000    2.3500
L PKFN TAUS    8.0000   32.0000    0.0000
L PKFN SIGM    4.0000    0.0000   12.9902    0.0000
L PKFN SWCH    1.0000    3.5136    0.6787
L RELA 1 1.0 La1 Z 1.0 Sr1 Z
L RELA 1 1.0 La2 Z 1.0 Sr2 Z
L RELA 1 1.0 La1 ITF 1.0 Sr1 ITF
L RELA 1 1.0 La2 ITF 1.0 Sr2 ITF
Z L RELA commands for the SITE occupancy variations (these set by
Z stoichiometric considerations)
L RELA 1 1.0 La1 SITE -1.0 Sr1 SITE
L RELA 1 1.0 La2 SITE -1.0 Sr2 SITE
L RELA 1 1.0 La2 SITE -0.5 La1 SITE
L VARY ONLY SCAL 1 BACK 1 BACK 2 BACK 3 BACK 4 BACK 5
L VARY A* C*
L VARY ZERO 1
L VARY ALL XYZ
```

```
L VARY SIGM 2
L VARY ALL ITF
Z Variation of SITE occupancies
L VARY La1 SITE La2 SITE
L VARY O1 SITE O2 SITE
* ... and reflections ...
```

χ^2 : 293.8473 → 35.2920 → 35.0318 → 35.0077

This essentially completed the refinement of this LAD data, and as can be seen from the χ^2, the refinement is fairly stable. The reason for the large χ^2 is that the expected R-factor R_E for these data is ~1%, meaning that the weighted profile R-factor R_{wP} is of the order of 6%. This represents a fairly good fit of the observed and calculated data, but the χ^2 looks high because it is expressed as $(R_{wP}/R_E)^2$. The final profile fit from this refinement is shown in the Figure overleaf, and the final LASRCU.CCN is also given overleaf.
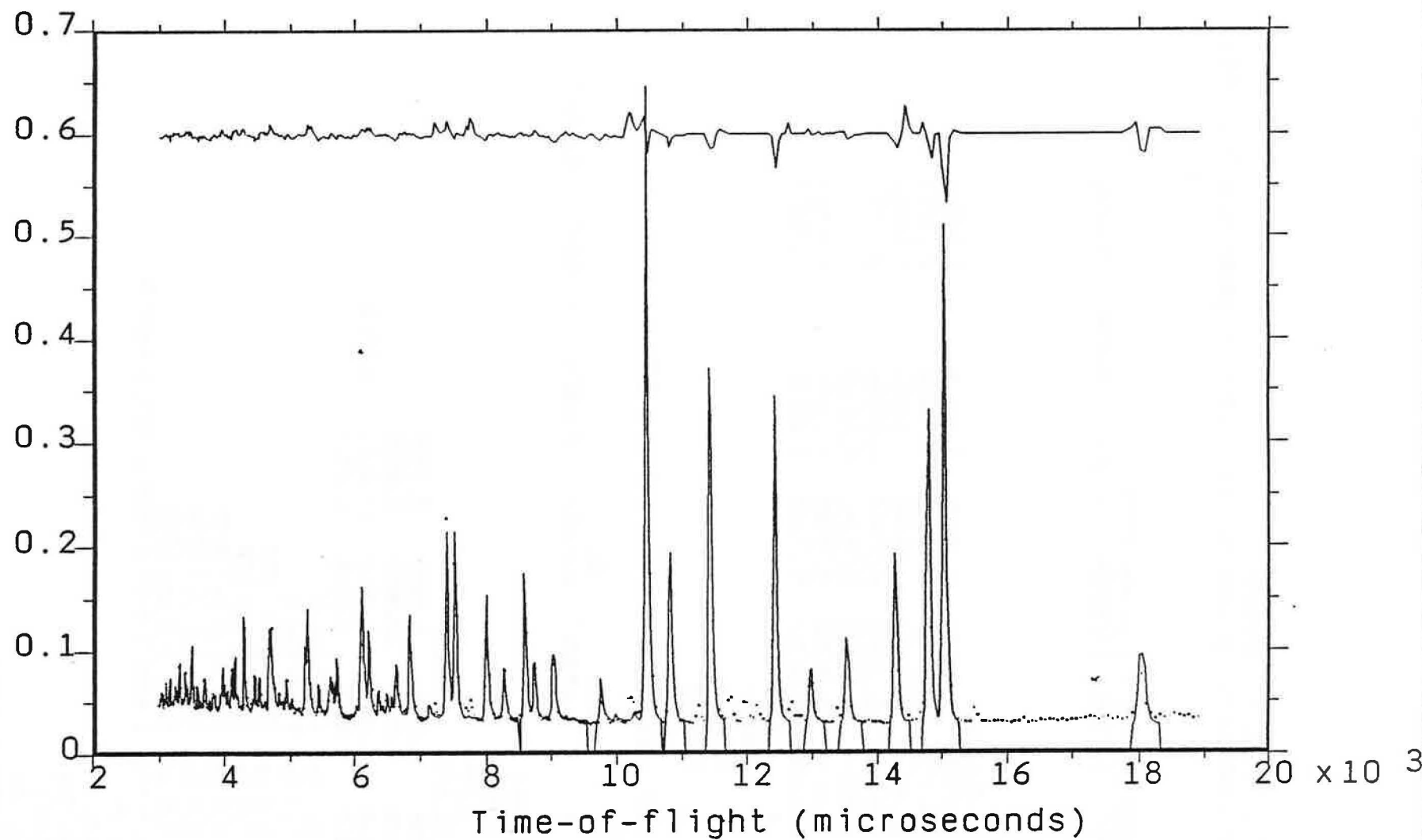
2.1.7 <u>The final parameter file</u>

The final LASRCU.CCN, giving the final refined parameters from this problem.

```
N La2SrCu206 LAD run 902 I4/mmm (139)
C    3.85860    3.85860   19.95785      90.000      90.000      90.000
S -X,-Y,Z
S -Y,X,Z
S -X,Y,-Z
S -X,-Y,-Z
S 1/2+X,1/2+Y,1/2+Z
A La1    0.00000    0.00000    0.00000    0.54139       1.08265
A Sr1    0.00000    0.00000    0.00000    0.54139      -0.08265
A La2    0.00000    0.00000    0.17860    0.30164       0.45868
A Sr2    0.00000    0.00000    0.17860    0.30164       0.54132
A Cu     0.00000    0.00000    0.59306    0.32330
A 01     0.00000    0.50000    0.08589    0.57277       0.99471
A 02     0.00000    0.00000    0.70123    1.37111       1.01263
F La       1    0.82700
F Sr       1    0.70200
F Cu       1    0.77180
F O        1    0.58050
B BOND
I NCYC 4 MCOR 0 PRIN 0 PRFO 0 PRPR 2 PRFC 0 BMIN 0.0 BMAX 3.0
L REFI -11
L RTYP    1       2000.         0.
L BACK    2        0.05320     0.00459     0.00019     0.00000     0.00000
L WGHT 3
L THE2 150.000
L SCAL   0.00345
L ZERO    7.1543
L PKCN   11.0700      0.0000
L PKFN TAUF    8.0000     0.0000     2.3500
L PKFN TAUS    8.0000    32.0000     0.0000
L PKFN SIGM    4.0000     0.0000    13.0466      0.0000
L PKFN SWCH    1.0000     3.5136     0.6787
L RELA 1 1.0 La1 Z 1.0 Sr1 Z
L RELA 1 1.0 La2 Z 1.0 Sr2 Z
L RELA 1 1.0 La1 ITF 1.0 Sr1 ITF
L RELA 1 1.0 La2 ITF 1.0 Sr2 ITF
L RELA 1 1.0 La1 SITE -1.0 Sr1 SITE
L RELA 1 1.0 La2 SITE -1.0 Sr2 SITE
L RELA 1 1.0 La2 SITE -0.5 La1 SITE
L VARY ONLY SCAL 1 BACK 1 BACK 2 BACK 3 BACK 4 BACK 5
L VARY A* C*
L VARY ZERO 1
L VARY ALL XYZ
L VARY SIGM 2
L VARY ALL ITF
L VARY La1 SITE La2 SITE
L VARY 01 SITE 02 SITE
* ... and reflections ...
```

The main conclusion from this refinement was that all the Sr in the structure in fact resides on the (La2,Sr2) site, with the zero (in fact negative) occupancy of Sr1 being quite conclusive. This result was at variance with some earlier work on this material.

2.1.8 Use of bond length calculations

This could be confirmed by performing a bond length calculation using the command BONDS and using the last LASRCU.CCN file as input. The BONDS procedure interprets the B BOND card in the file and uses BMIN and BMAX to set limits for the scan. The resulting bond lengths are summarised below:

Interatomic distances calculated from BONDS program for LASRCU example

Atom1-Atom2	Bond length (Å)
La1 – O1	2.5808
Sr1 – O1	2.5808
La2 – O1	2.6732
La2 – O2	2.7656
La2 – O2′	2.3983
Sr2 – O1	2.6732
Sr2 – O2	2.7656
Sr2 – O2′	2.3983
Cu – O1	1.9346
Cu – O2	2.1588
O1 – O1	2.7284

As can be seen from this the bond lengths to O1 from the Sr occupied site (La2,Sr2) are somewhat longer than from the La1 site, which makes chemical sense since Sr is a larger ion than La. This demonstrates the use of chemical information contained in bond parameters to verify the results of a refinement.

CRYSTAL STRUCTURE PLOTTING PROGRAMS

SECTION 6

1 <u>INTRODUCTION</u>

There are four structure plotting programs currently available, three are interactive and the fourth non-interactive, these are CHEM-X, ORTEP, PLUTO78 and STRUPLO. The programs are initiated by typing the appropriate name at a terminal session (eg ORTEP), following this you will be presented with at least the option of using an existing graphics data set in the appropriate format or converting an existing CCSL data file to produce another file containing the crystallographic data in a format appropriate for the graphics program. In the case of STRUPLO the formated file *.STR, will need to be edited to add the appropriate plotting commands. The CHEM-X session begins after the *.NTH file has been read and displayed. The ORTEP session commencies with the user issuing the appropriate commands to read in the data from the *.ORT data file. The PLUTO78 session begins after the graphics output device has been nominated. A short description of the programs, followed by a more detailed description of the commands, example data files, and example plots for the zeolite ferrierite are given below.

CHEM-X

This is a sophisticated commercial molecular modelling package produced by Chemical Design[1], which apart from colour representation with real time manipulations on high-performance terminals, can also be used to carry out sophisticated energy calculations, conformational analysis, molecular fitting and drawing of contour surfaces. Without the sophisticated colour terminals, it can still be used to generate stick, ball and spoke and space filling illustrations allowing rotation, scaling, deletion of atoms and bonds, geometry calculations etc.

ORTEP

This is the interactive version, part of the GX crystallographic program system of Glasgow[2], which is modified from the original Ortep program written by Johnson[3]. The most important feature is the drawing of thermal ellipsoids, in addition to stick, ball and spoke, perspective views and stereoscopic views and deletion of atoms.

PLUTO78

This is the interactive version developed at Rutherford[4] of the original program written by Motherwell[5]. Its sophistication is intermediate between CHEMX and ORTEP, it allows stick, ball and spoke and space filling representation with the facility of shading, half-tone, rotation, scaling, stereoscopic views and colour output.

STRUPLO

This is a non-interactive crystal structure plotting program by Fischer[6] the most significant feature of which is the representation of polyhedra, specifically tetrahedra and octahedra cation coordinations. Rotation, scaling, stick representations and circular atoms can be drawn.

2 CHEM-X COMMANDS

There are a great number of commands available and are presented in the CHEM-X reference manual (which is almost 6 inches thick!). Only the simplest commands are presented here, these allow displaying of the structure, rotation, repacking, deletion of atoms and the presentation of different drawing styles.

(HEL)P

At all times when the prompt (*) is showing, help on the available commands may be obtained by typing this command. If information on a specific command is desired, the command followed by a question mark eg READ ?, will initiate help text for the specific topic.

(EXI)T/(NOL)OG

Terminates the CHEM-X session.

(REA)D/(WRI)TE

The initial data file *.NTH is in a 'NORTH' format, thus to read in this file the command READ (NOR)TH {file.NTH} is given. If no space group for the structure is available, a command file *.SYM, containing symmetry information will have being produced in the process of reformatting the CCSL file, the command READ (COM)MAND {file.SYM} will read this in. Pictures may be saved, preserving the current view etc. as seen, by writing to an ARCHIVE file *.ARC using WRITE (ARC)HIVE {file.ARC}, and subsequently read in by READ ARCHIVE {file.ARC}.

SET PACK/(MOD)IFY

Display of the structure without any other instructions will show only the asymmetric unit specified in the data file. Packing of the structure using the symmetry information specified by SET PACK allows more of the structure to be shown. Thus SET PACK /(SP)ACE GROUP {group}, specifies the space group for which all the symmetry information will be provided by CHEM-X, SET PACK /RANGE {xmin xmax ymin ymax zmin zmax}, will specify the range of the unit cell that will be built up by CHEM-X. SET PACK /(WIN)DOW {xmin xmax ymin ymax zmin zmax}, will specify the amount of the unit cell specified by /RANGE that will actually be displayed. Once the symmetry information and the packing ranges have been defined, the packing of the structure may be initiated by the command MODIFY /PACK. A new range may be packed by deleting the current packed atoms using MODIFY /(NOSY)MMETRY, specifing a new range and then repacking the structure.

(DIS)PLAY

The structure may be displayed by this command, different styles from the default are obtained by DISPLAY (STI)CK for stick drawing, no atoms drawn, DISPLAY (SOL)ID/(BON)DS or DISPLAY (SOL)ID/(NOBON)DS to display ball and spoke or space filling style.

(ROT)ATION x y z

Rotation of the structure is specified by the angles x,y,z in degrees eg 90 0 0.

(MOD)IFY/(CUR)SOR

The command MODIFY/CURSOR initiates the appearance of a graphical cursor and a abbreviated menu. In this mode individual atoms may be deleted and specified bond lengths, bond angles and torsion angles may be calculated using the cursor to select the appropriate atoms followed by single key commands. This mode is terminated by a full stop '.' and information on the available options may be obtained by typing a question mark.

(NOM)INATE (DES)IGN

The command NOMINATE DESIGN allows the current displayed picture to be
saved on file for later output on the laser printer. After issuing this
command, it should be followed by DISPLAY which will save the picture in
a file Username.DES, further terminal display is resumed by the command
NOMINATE VT100. On exiting from CHEMX, all the saved pictures of the
session will be contained in one *.DES file, they may be output to the
terminal by the command CHEMVDU or to the laser printer by CHEMLAS.
These two commands will produce a laser.dat file containing the graphics
output which may be used to produce further copies to the laser printer.

2.1 CHEM-X NORTH DATA FILE

The date contains entries that are given in free format, each line being
presented in the specified order.

    * 0 CELL a b c alpa beta gamma

This provides information on the cell parameters

    * 2 title

This provides a title for the structure

    at1 x y z
    at2 x y z
    .

    .

The list of atom specifications involves an atom label and the
fractional atomic coordinates

CHEM-X NORTH FILE

```
* 0 CELL      18.620      14.124      7.382      90.000      90.000      90.000
*   2 N FERRIERITE
Si1     0.15402     0.00000     0.00000
Si2     0.08447     0.20381     0.00000
Si3     0.27485     0.00000     0.28095
Si4     0.32270     0.20183     0.20331
O1      0.00000     0.18837     0.00000
O2      0.25996     0.00000     0.50000
O3      0.09903     0.08867     0.00000
O4      0.20034     0.00000     0.18398
O5      0.25000     0.25000     0.25000
O6      0.35275     0.22858     0.00000
O7      0.11303     0.26116     0.17418
O8      0.32193     0.09171     0.23475
```
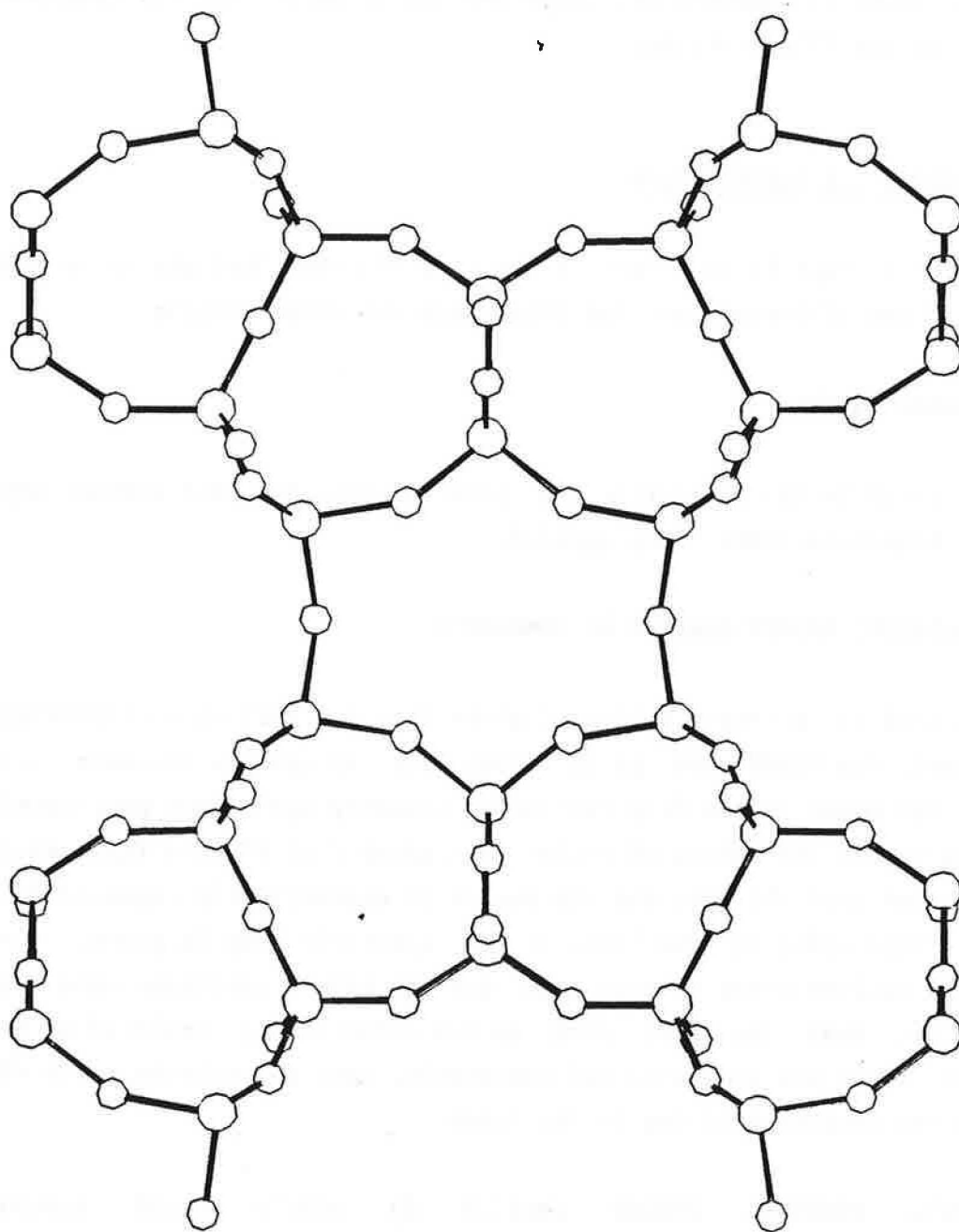
(see figure 11)

Fig 11 CHEM-X plot of N Ferrierite

3 ORTEP COMMANDS

The interactive Ortep commands are presented as a menu and fall into to two categories: i) Commands for composing the illustration. ii) Commands for drawing the illustrations.

3.1 COMPOSING THE ILLUSTRATION

i) The first stage is to 'read' in the list of atoms that are to be the subject of the illlustration. For this there are three options.

(MOD)EL INSERT

All the atoms in the model file are inserted into the list without any symmetry transformations being applied.

(MOL)ECULE INSERT dmx(2.0 Å) SYMMETRIC

This is used to to create a list of atoms that are part of a chemically bonded set. The **FIRST** atom in the model file is used to initiate the search, all atoms in the file (including symmetry-equivalent positions) that are within the sphere of enclosure (radius dmx) of this first atom are inserted into the list and the search is automatically repeated for all the atoms added to the list. If the symmetric flag is given, the list will include atoms in more than one equivalent position. Care has to be taken that the first atom is not structurally isolated or no connected atoms are generated and conversely, that an infinite chain of atoms is not generated if dmx is too large.

(CEL)L CONTENTS INSERT dmx(2.0 Å) x(0.5) y(0.5) z(0.5)

Atoms in the model file are inserted into the list if, after any

necessary symmetry transformations, they lie within the range (1/2+x:1/2-x, 1/2+y:1/2-y, 1/2+z:1/2-z) of the unit cell, where x,y,z refer to the unit vectors of the unit cell. dmx specifies a bond length which allows atoms connected to those inside the defined range to also be included until complete molecules are obtained. It is important to ensure that a very small value of dmx is given if only those atoms within the specified range are to be included or for a fully connected structure like a zeolite.

ii) The next stage if desired, is to modify the list of atoms, their orientation and scale.

(DEL)ETE at1 at2 at3 ..

This deletes atoms from the list, including all equivalent positions. at1, at2 .. can be a specific atom label eg SI(1) which deletes the specified atom, or atom type eg SI which removes all atoms of that type.

(ROT)TATE axis angle

This rotates the reference axis X,Y,Z by the specified angle, positive for anti-clockwise rotation viewed along the positive end of the axis. Successive rotation commands are cumulative. The initial orientation defines a parallel to x and z parallel to c, where x y and z are directions on the screen are as defined by the command BEST VIEW.

(SCA)LE mod ell(1.54)

With no parameters this scales the illustration as described under BEST VIEW. Alternatively this specifies an explicit scale factor in inches/Å of the figure and/or a probability ellipsoid. To change the ellipsoid scale only, a comma should be given in place of the first parameter.

(SIZ)E ele/ALL rad(0.1)

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Defines a sphere size in Å for the given type of atom or if ALL is given, for all atoms. This overrides any given temperature factors.

(BES)T VIEW

This defines a set of reference axes in the crystal which parallel the axes of the graphical device. The reference x and y axes are horizontal and vertical respectively, lying in the least-squares plane through the atoms in the list, the z axis at right angle to this plane. The origin and scaling of the illustration will be automatically chosen for the 'best view'. It is wise to issue the command best view after forming the list of atoms in order to get a suitable starting point for subsequent reorientation.

3.2 DRAWING THE ILLUSTRATION

These are commands that are performed when the figure is drawn, they may be categorised into two types: i) Device and program control commands, ii) Drawing style.

3.2.1 Device and program control

(SAV)E SEQUENCE

Opens the start of a saved sequence of display commands that can be executed together as one command, which replaces any previously-defined sequence.

(END) SAVED SEQUENCE

Marks the end of a saved sequence.

(EXE)CUTE SAVED SEQUENCE

Causes all commands between SAVE and END of the current saved sequence to be performed.

(STE)REO sep

Causes the current saved sequence to be performed twice, with stereoscopic rotations of the viewpoint. The separation parameter is the distance in inches between left and right-eye views, usually 2.5.

(NEW) PLOT dist(30 inches) x

This prepares for a new drawing, for example after ROTATE. The origin point of the current device will be shifted along the x axis if the x parameter(inches) is given (positive or negative). The perspective distance can also be changed from the default, 0.0 signifies a parallel projection.

(PLOT)TER

Defines the current graphical output to be a hard copy device. In this case any graphical output is stored in a laser.dat file for subsequent output on the laser printer.

(VDU)

Defines the current graphical output to be to the screen.

(MEN)U ON/OFF

Inverts the setting of the menu switch, initially on. The menu of commands is displayed each time the VDU or NEW PLOT command is issued.

3.2.2 <u>Drawing style</u>

```
(BON)DS shad rad over<cr>
ele ele (shad rad)<cr>
    .         <cr>
    .         <cr>
              <cr>
```

Causes bonds to be drawn between all pair of atom types in the element pair list. This list consists of two atom types (eg SI, O) on each line. The end of the list is signified by a blank line. Covalent radii used to define the bond lengths are contained in the programs data file. The shading and thickness of the bond and the overlap gap between obscured and visible parts of the figure are controlled by the respective parameters. The shading parameter is in a range of 1-5, the bond radius is in Å and the overlap gap is in inches. Line bonds are drawn if the shading and radius parameters are omitted. Different bond styles for different kinds of bonds by including the shading and radius parameters in the element pair list.

(ATO)MS PLAIN/UNSHADED/SHADED ele

Causes the specified atom types to be drawn, the style of the drawn atom is the boundary ellipse (PLAIN), boundary ellipse plus principal ellipses (UNSHADED) and boundary plus principal ellipses plus octant shading.

(LAB)EL AXES/ele/ALL x(0.0) y(0.0)

Places labels on the unit cell axes, on atoms of the given type, or on all atoms. x and y specify the offset of the label along the axis or from the centre of the atom.

(OUT)LINE

Draws the outline of the unit cell, provided it is in within the current drawing area. Rescaling may be achieved by using OUTLINE followed by SCALE and then OUTLINE again.

3.3 ORTEP CRYSTAL MODEL FILE

The entries are in free-format prefixed by the name of the type of information given, entries may be continued on the next line by terminating the current line by a space and the equals symbol '='. Items within a line may be separated by spaces or commas, and a comma may be used to denote default values.

TITLE title

CELL a(1.0) b(1.0) c(1.0) alpha(90.0) beta(90.0) gamma(90.0)

Unit cell parameters in Å and degrees.

LATT centrosymm(C) type(P)

Defines centrosymmetric C or non-centrosymmetric A and the lattice type P, I, R, F, A, B, or C.

SYMM x y z

These specify the general position coordinates as given in the International Tables eg -Y,1/2+X,Z; the three coordinates being separated by commas, (spaces are ignored). Lattice translations, centre of symmetry and X,Y,Z should not be given.

ATOM label x y z occupancy u11 u22 u33 u12 u13 u23 n

These define the atoms in the asymetric unit, the label consists of the

element name (uppercase) followed by any other characters in brackets e.g. SI(1) up to a total label length of 8 characters; x,y,z are in fractional coordinates. The occupancy is irrelevant for graphical output and should be given a value of 1.0, u11, u22 etc are the anisotropic temperature factors assumed to be isotropic temperature factor if only one value given.

ORTEP DATA FILE

```
TITLE N FERRIERITE
CELL    18.6199    14.1236    7.3816    90.0000    90.0000    90.0000
LATT C I
SYMM X,Y,Z
SYMM -X,Y,-Z
SYMM X,-Y,-Z
SYMM -X,-Y,Z
ATOM   SI(1)     0.1540     0.0000     0.0000    1.0000 -
0.012 0.009 0.019 0.0 0.0 0.0
ATOM   SI(2)     0.0845     0.2038     0.0000    1.0000 -
0.008 0.014 0.013 0.0 0.0 0.0
ATOM   SI(3)     0.2749     0.0000     0.2810    1.0000 -
0.023 0.013 0.016 0.0 -0.007 0.0
ATOM   SI(4)     0.3227     0.2018     0.2033    1.0000 -
0.016 0.015 0.013 -0.0012 -0.0015 -0.001
ATOM   O(1)      0.0000     0.1884     0.0000    1.0000 -
0.001 0.036 0.04 0.0 0.0 0.0
ATOM   O(2)      0.2600     0.0000     0.5000    1.0000 -
0.044 0.035 0.019 0.0 0.0 0.0
ATOM   O(3)      0.0990     0.0887     0.0000    1.0000 -
0.032 0.021 0.1 0.006 0.0 0.0
ATOM   O(4)      0.2003     0.0000     0.1840    1.0000 -
0.032 0.11 0.023 0.0 -0.016 0.0
ATOM   O(5)      0.2500     0.2500     0.2500    1.0000 -
0.038 0.04 0.06 0.022 0.001 -0.008
ATOM   O(6)      0.3528     0.2286     0.0000    1.0000 -
0.056 0.052 0.014 -0.005 0.0 0.0
ATOM   O(7)      0.1130     0.2612     0.1742    1.0000 -
0.035 0.066 0.038 -0.008 -0.016 -0.029
ATOM   O(8)      0.3219     0.0917     0.2348    1.0000 -
0.053 0.019 0.058 0.003 0.01 0.015
```
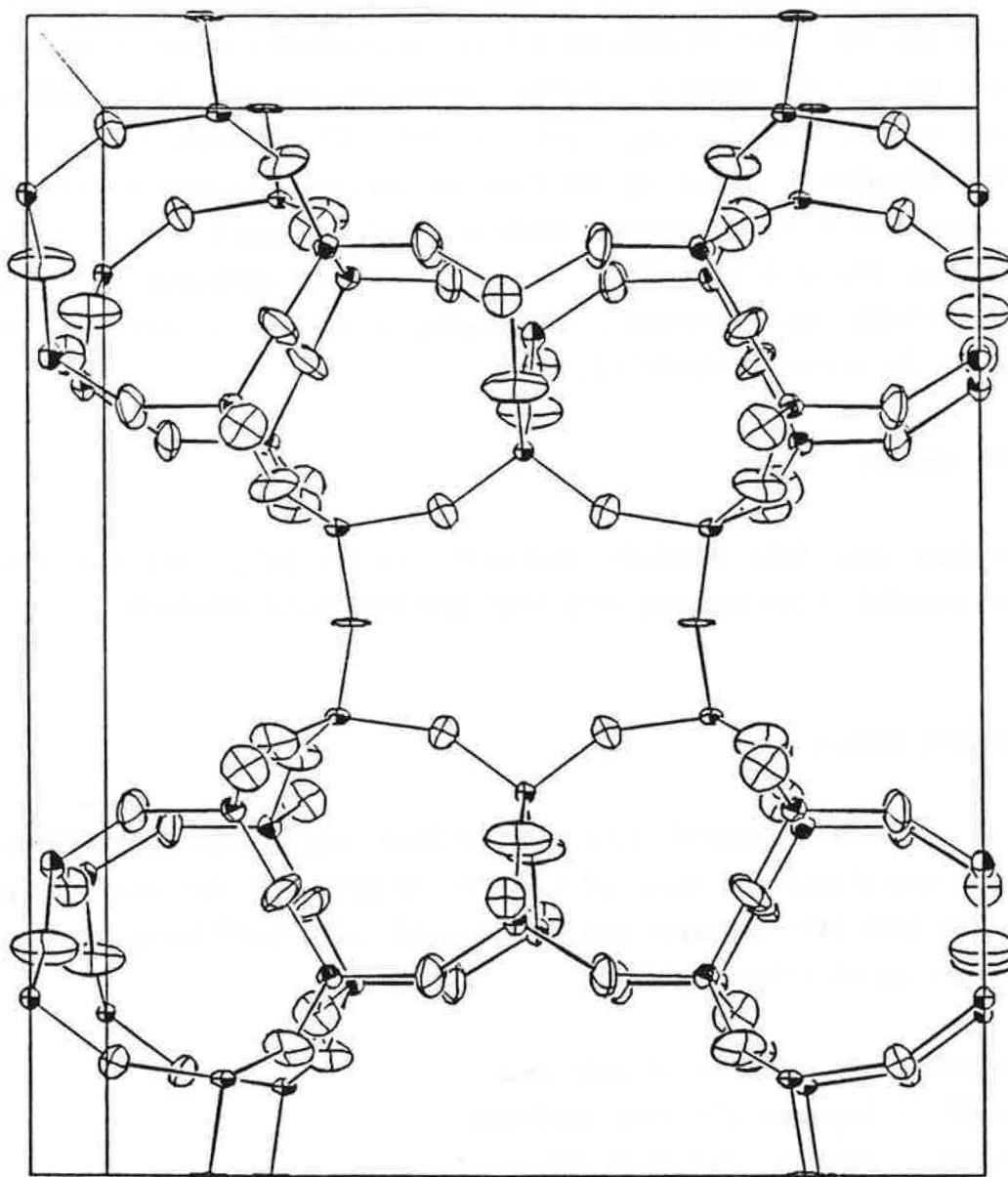
(see figure 12)

Fig 12 ORTEP plot of N Ferrierite

4 PLUTO78 COMMANDS

There are a fair number of commands available at an interactive session and these are explained in more detail in the PLUTO78 reference manual. The first part of the session involves answering the prompts to define the graphics output device (eg. laser or terminal), specifying if the data file contains a single or multiple dataset and specifying if all the datasets will be processed using a single command set or many command sets. The next part of the session involves defining the style of and plotting the structure by issuing a series of commands in response to the prompt COMMAND? ->.

HELP command

HELP invokes the help facility and will provide help text for the requested command, HELP COMMAND will list the available commands.

OPT/GOPT keword

(G)OPT is the first command in a command list and resets the various flags and variables for this plot (OPT) or globally for all plots (GOPT). The OPT/GOPT command may be repeated with qualifying kewords defining various plotting styles:-

    CELLPLOT - Plot outline of unit cell
    NOLABEL - Suppress all atom labelling
    NOTITLE - Suppress output of title
    SOLID   - Plot ball and spoke model
    STEREO   - Plot side-by-side stereo pair
    VIEWX   - View along x axis
    VIEWY   - View along y axis

VIEWZ   - View along z axis

PERSP d(600.0)

The PERSP command provides a perspective view from a viewpoint d mm from the crystal model.

RADII ATOMS/BONDS el1 r1 el2 r2 ..

The RADII command is used with the (G)OPT SOLID option and specifies the radii of atom circles or bond cylinders. eln rn are specific atom types and associated radii in angstroms. A number of other options are available including:- RADII BONDS ALL r m defining all bonds with radius r using m lines and RADII BONDS TAPER t provides a taper in the bonds according to the tapering parameter t (1-20).

RANGE xmin xmax ymin ymax zmin zmax

RANGE specifies the packing of more than one unit cell in the plot were xmin xmax etc. define the packing ranges in terms of unit cell translations.

VIEW X0/Y0/Z0 XROT a YROT b ZROT c

The VIEW command overides the initial view defined in the (G)OPT command and provides the options of views along the x, y, or z axis with rotations in degrees around these axis.

SHADE a1 a2

SHADE causes the drawing of shade lines representing shadow from a light source defined by the two angles a1 and a2 in degrees. Assuming that XP and YP correspond to the x y plane of the graphics device and ZP is perpendicular to this plane, then a1, a2 correspond to the rotation of

the light source about YP and ZP respectively. a1 = a2 = 0 corresponds
to light coming directly towards the viewer, so that the whole atom is
shaded and a1=100, a2=-60 provides approximate half-shading.

PLOT ENTNO c

The PLOT command initiates the plot and is the last command in a command
list, the ENTNO qualifier defines which entry c in a multiple dataset is
to be plotted

STOP

The command STOP terminates the program.

4.1 PLUTO78 DATA FORMAT

Data defining the crystal structure can be in two formats, the Cambridge
database format or in free-format. The free-format data is the easiest
to set up from a terminal session and is illustrated below. As expected
in this form all entries are free-format except for the keywords which
should start in column 1.

TITLE title

Up to 74 characters.

CELL a(1.0) b(1.0) c(1.0) alpha(90.0) beta(90.0) gamma(90.0)

Unit cel parameters in Å and degrees.

SYMM x y z

These specify the general equivalent positions as given in the
International Tables for X-ray Crystallography, volume 1, eg.

-Y,1/2+X,Z.

The full set of positions are required including centre of symmetry if present and lattice centring, the first set in the list must be X, Y, Z.

label x/a y/b z/c

These define the atoms in the asymetric unit, the label consists of two parts, the first is the chemical symbol and the second a number to identify each atom of a particular type. The total length of the label must be 6 characters or less. Atomic positions are given as fractional coordinates.

END

This indicates the end of the current data entry.

PLUTO78 DATA FILE

TITLE FERRIERITE
CELL   18.6199   14.1236   7.3816   90.0000   90.0000   90.0000
SYMM X,Y,Z
SYMM -X,Y,-Z
SYMM X,-Y,-Z
SYMM -X,-Y,Z
SI1   0.1540   0.0000   0.0000
SI2   0.0845   0.2038   0.0000
SI3   0.2749   0.0000   0.2810
SI4   0.3227   0.2018   0.2033
O1   0.0000   0.1884   0.0000
O2   0.2600   0.0000   0.5000
O3   0.0990   0.0887   0.0000
O4   0.2003   0.0000   0.1840
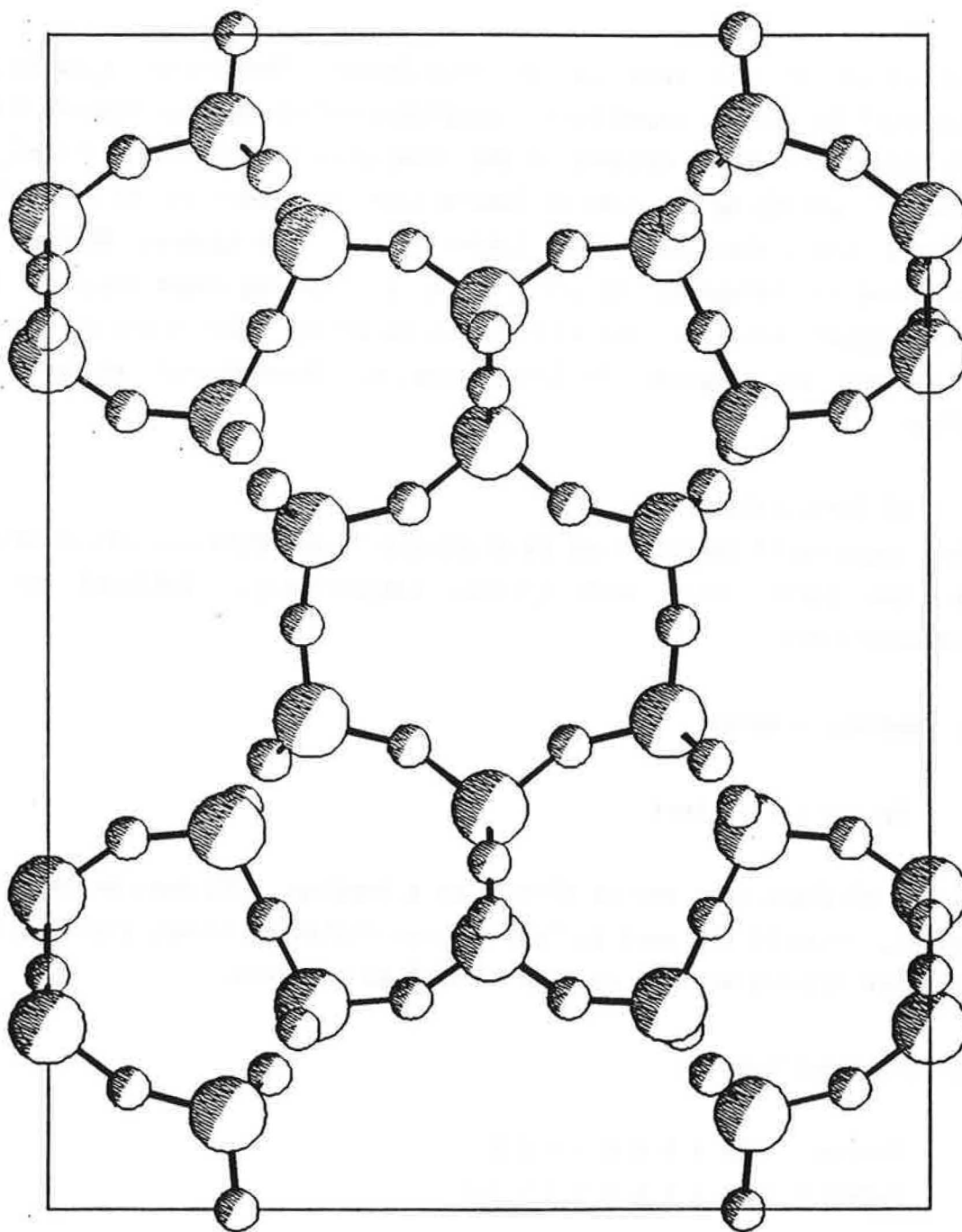O5   0.2500   0.2500   0.2500
O6   0.3528   0.2286   0.0000
O7   0.1130   0.2612   0.1742
O8   0.3219   0.0917   0.2348
END

(see figure 13)

Fig 13 PLUTO78 plot of N Ferrierite

5 STRUPLO DATA FILE INSTRUCTION COMMANDS

The input of all data is in free format. Numbers or symbols are separated by blanks, typed in any arbitrary column between columns 5 and 80. The first four columns of the instruction data are provided for options specifying the type of instruction. Any text in the first four columns other than the options listed here will be ignored. Numbers can be given as integers, floating point or floating comma numbers; all three types will be transformed to floating point numbers. Atomic parameters may begiven in free format or fixed format as described below.

a) Instructions

The sequence of instructions is arbitrary except TITL and END whichmust be the first and last option, respectively, followed by the atomparameters.

1. Heading, comment

Option : TITL text

Up to 80 characters can be plotted as a heading. TITL must be the first option, even if the text is left blank. Following lines, starting with TITL are without action, but can be used as comments.

2. Plot specification

Option : PARA A B C D E F G H
Default: PARA 1 1 1 1 1 1 1 3.2

A) Scale factor

The plot is scaled to the full width of the paper, leaving a margin for the heading. Scale factors > 1 will cut off the drawing, but might be desired in special cases.

B) Index for center in origin

= 0 no center in the origin
= 1 centrosymmetric with center in the origin

C) Index for outlines of unit cell

= 0 no outlines
= 1 outlines cell

D) Index for type of representation

= 0 skeleton model

This representation, often used for framework structures, shows only the connections between the centers of neighbouring polyhedra.

= 1 polyhedral representation

Tetrahedra and octahedra are sought by the program within the limits given in options TETR and OCTA. All polyhedra are hatched with equidistant lines parallel to that edge of the triangle which is opposite the vertex with the highest Z-coordinate. In this way the density of hatching illustrates the inclination of a polyhedral face.

E) Index for tetrahedra

= 0 no tetrahedra
= 1 tetrahedra are sought and drawn within the values given in option TETR. The default values correspond to average Si-O distances.

F) Index for octahedra

= 0 no octahedra
= 1 octahedra are sought and drawn within the values given in option
OCTA. The default values correspond to average (Na, Ca)-O distances.

If lines are drawn belonging neither to tetrahedra nor octahedra the
default parameters have to be changed in option TETR or OCTA.

G) Index for program execution

= 0 only tables with atomic coordinates and distances and angles are
printed, no plot is produced.
= 1 tables with atomic coordinates and distances and angles are printed
and a projection of the crystal structure is drawn.

H) maximum value for interatomic distances to be calculated.If more than
100 distances up to the value H are calculated the execution of the
program will be terminated. In this case the maximum distance should be
given a lower value.

4. Cell constants

    Option : CELL a b c alpha beta gamma
    Default: CELL 10 10 10 90 90 90

The cell constants are expected in Å and degrees.

5. Space group symbol

    Option : SPGR space group symbol
    Default: SPGR P1-

Only the Bravais type is interpreted in this version of STRUPLO. The

space group symbol does not replace the symmetry operators given in options SYMM.

6. Symmetry operators

    Option : SYMM symmetry operators
    Default: SYMM X,Y,Z

Each line beginning with SYMM contains several operators separated from each other by a semicolon. The last symbol in a line must not be a semicolon. Translations are given as fractions (1/2, 2/3 ...).identity operator x,y,z; centrosymmetric counterparts and lattice translations are not required. The syntax is consistent with the syntax in the International Tables for Crystallography.

7. Format for atomic parameters

    Option : FORM A
    Default: FORM 4

A format index; note that in all cases the atom name is read in A2, I2.

= 1 reads a SHELX parameter file (not instructions) including FVAR and interprets constraints. This part of the program has been taken from the 1983 version of STRUPLO and could not be tested in the current form. Check carefully possible errors]

= 2 Format (2A1, I2, 26X, 3F10.6) corresponding to the input format of the atomic parameters in the least squares program ORFLS.
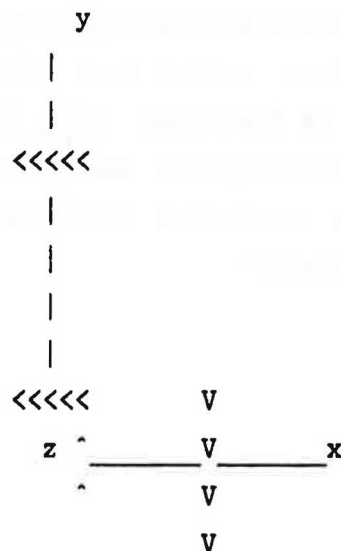= 3 Format (2A1, I2, 3F10.6)
= 4 free format. An atom name consisting of two letters is expected in the first two columns, followed by a sequence number and the X,Y,Zcoordinates.

8. Rotation

```
Option : ROTA A B C
Default : ROTA 0 0 0
```

A, B, C are rotation angles around the orthogonal axes X,Y,Z, with the origin in lower left corner, X pointing right, Y pointing up,Z sticking out. The sense of rotation is shown in the following graph.

```
                        y
                        |
                        |
                      <<<<<
                        |
                        |
                        |
                        |
                      <<<<<        V
                  z ^             V        x
                    ^_____V_____
                                  V
                                  V
```

Z is parallel to the crystallographic c-axis,
Y is the trace of the crystallographic b-axis in the plane perpendiculor to Z,
X is parallel to Y x Z.

9. View direction

```
    Option : VIEW X1 X2 X3 Y1 Y2 Y3
    Default: VIEW 0 0 1 0 0 0
```

Instead of option ROTA, VIEW can be used to specify a view direction X and Y are coordinate triples, where the vector defining the view direction points from X to Y. If Y is not given, the origin 0,0,0 is assumed. The space diagonal of a unit cell, for instance, would be

defined by VIEW 1 1 1 . This routine does not adjust one of the crystallographic axes paral-lel to the edge of the paper and the plot will have an arbitrary orientation around the orthogonal Z-axis. This can be corrected bya subsequent run, where the rotation angles are taken from the output data as calculated by VIEW. Adding now a third rotation angle in option ROTA and omitting VIEW will give a better orientation

11. Range in X, Y, and Z directions

        Option : XYZR A1 A2 B1 B2 C1 C2 D1 D2 E1 E2 F1 F2
        Default: calculated by program

All data given here refer to the unit vectors of the unit cell. A1 A2, B1 B2, C1 C2 are minimum and maximum range (X,Y,Z) for polyhedra, D1 D2, E1 E2, F1 F2 are the X,Y,Z components for the range in which circles are to be drawn defined in CIRC. The range for the circles must lie within the range for the polyhedra. If only the range for the polyhedra is given, this range will be taken also for the circles.

12. Circle specificationsion

        Option : CIRC R N1 N2 N3....
        Default: no circles

R   Radius\A\

N1...Atom names consisting of two letters corresponding to the names of the atomic parameters

'CIRC 0.8 NA CA' draws sodium and calcium atoms as circles with radius 0.8 A. The symbols listed in one line refer only to one radius which is always the first number in option CIRC.p to 10 different radii (= 10 options CIRC) are accepted. If circles appear not to be drawn completely, the value for the resolution of the plotter is probably too high.

13. Tetrahedra specifications

Option : TETR A B CD
Default: TETR 109201.620.2

A = tetrahedral angle
B = angle tolerance
C = mean distance from central atom to coordinated atoms
D = tolerance for C

Tetrahedra are sought and drawn with distances between central atomand vertices of C+-D \A\ and angles between central atom and two vertices of A+-B \deg\.

14. Octahedra specifications

Option : OCTAA B CD
Default: OCTA 90201.970.4

The same meaning as in 10.

15. Exclusion of atoms

Option : OMIT A B C D ...
Default: no atoms are excluded

A B C D refer to the numbers in parenthesis in the output listing. If the numbers follow each other in direct sequence they may be given as A -B, where A and B are first and last number in this sequence. With instruction 'OMIT 9 15 -18 23 26' atoms with sequence number 9, 15, 16, 17, 18, 23, 26 are excluded from the parameter list and will not be drawn. If an excluded atom belongs to a polyhedron the whole polyhedron will be omitted.

16. Hatching polyhedra

    Option : SHAD NLN1 N2 N3 ...
    Default: SHAD 9 1 -H(8)

With this option the number of lines NL for the hatching of a
poly-hedral face can be chosen. If NL is negative all polyhedra are left
blank. NL from 0 to 20 gives the number of lines per face of the
polyhedra N1 N2 N3 ... . These numbers refer to the sequence numbers of
the polyhedra as given in the output list on unit 6. For explanation of
the syntax see 15.

17. End of instruction list

    Option : END
    no default option

    b) atom parameters

STRUPLO expects 5 statements per atom

a) atom name, containing one or two letters

b) atom label, any number < 100

c) fractional coordinates only atoms in the asymmetric unit need be
given

STRUPLO DATA FILE

```
TITL N FERRIERITE
CELL    18.6199    14.1236    7.3816    90.0000    90.0000    90.0000
SYMM X,Y,Z
SYMM -X,Y,-Z
SYMM X,-Y,-Z
SYMM -X,-Y,Z
SPGR I***
XYZR -0.75 0.75 -0.75 0.75 -0.75 0.75
SHAD  9 1 -400
END
SI  1     0.15402    0.00000    0.00000
SI  2     0.08447    0.20381    0.00000
SI  3     0.27485    0.00000    0.28095
SI  4     0.32270    0.20183    0.20331
O   1     0.00000    0.18837    0.00000
O   2     0.25996    0.00000    0.50000
O   3     0.09903    0.08867    0.00000
O   4     0.20034    0.00000    0.18398
O   5     0.25000    0.25000    0.25000
O   6     0.35275    0.22858    0.00000
O   7     0.11303    0.26116    0.17418
O   8     0.32193    0.09171    0.23475
```
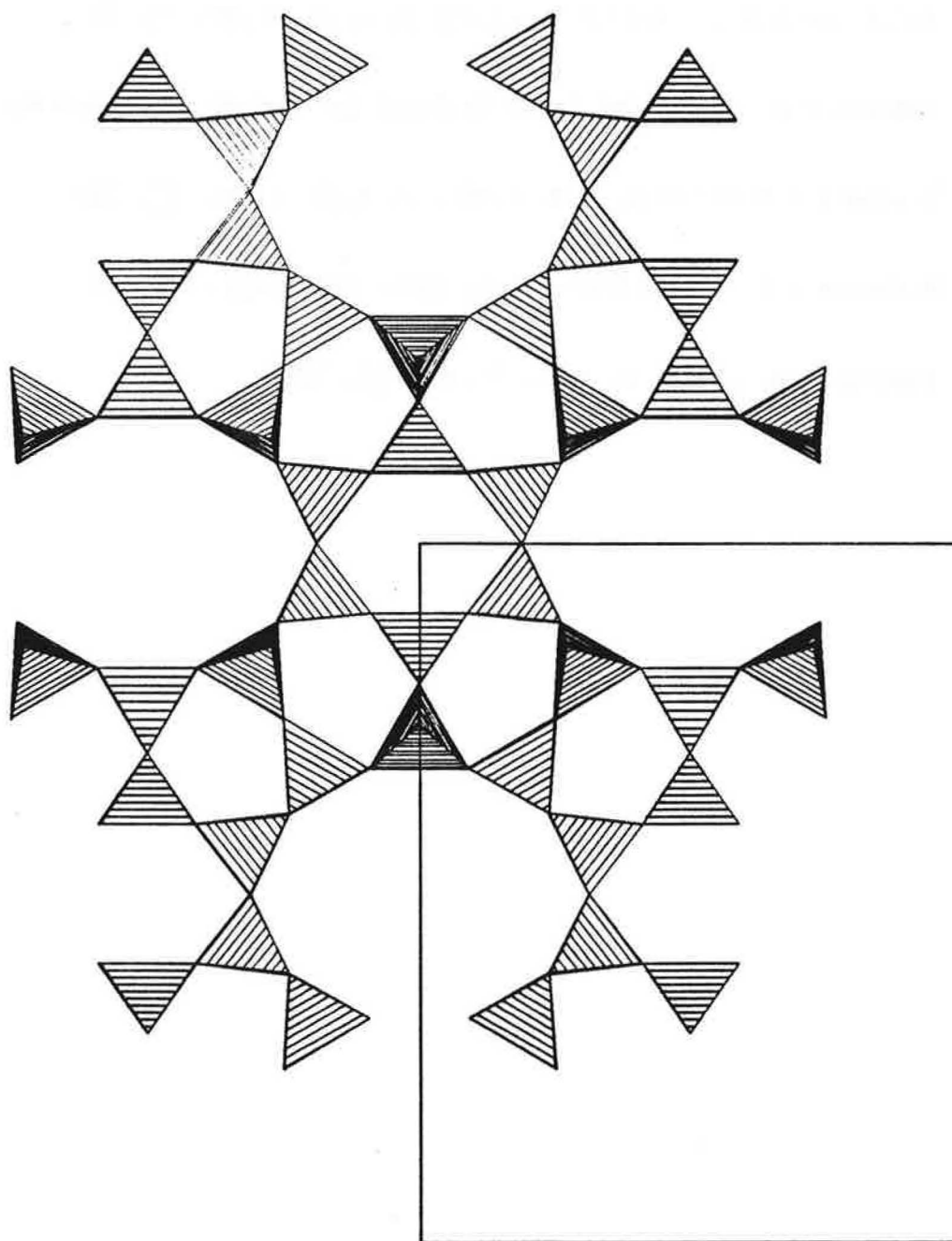
(see figure 13)

Fig 13   STRUPLO plot of N Ferrierite

REFERENCES

[1]   Chemical Design Ltd, Oxford, England.

[2]   Mallinson P R and Muir K W, (1985) J. Appl. Cryst. <u>18</u>, 51

[3]   Johnson C K, (1971) Oak Ridge National Laboratory of Tennessee.

[4]   Crennell K M and Crisp G M, (1984) J. Appl. Cryst. <u>17</u>, 366

[5]   Motherwell S, (1970) Univ. Chem. Lab., Cambridge, England.

[6]   Fischer R X, (1985) J. Appl. Cryst. <u>18</u>, 258.

APPENDICES

Appendix 1 - Chopper Offsets

Tmin (µs)	6m Chopper offset	9m Chopper offset
12000.00	39	817
15000.00	229	1101
20000.00	545	1575
25000.00	861	2049
30000.00	1177	2523
35000.00	1493	2997
40000.00	1809	3471
45000.00	2125	3945
50000.00	2441	4419
55000.00	2757	4893
60000.00	3073	5367
65000.00	3389	5841
70000.00	3705	6315
75000.00	4022	6789
80000.00	4338	7263
85000.00	4654	7737
90000.00	4970	8211
95000.00	5286	8685
100000.00	5602	9159
105000.00	5918	9633
110000.00	6234	10107
115000.00	6866	11055
120000.00	6945	11174
125000.00	7182	11529
130000.00	7498	12003
135000.00	7814	12477
140000.00	8131	12951
145000.00	8447	13425
150000.00	8763	13899
155000.00	9079	14373
160000.00	9395	14847

If the required Tmin is not listed, it may be calculated, remembering that the offsets are of the form A+B(Tmin), where A and B are constants.

ie. Offset(6m) = 0.063213*(Tmin) - 719.2

Offset(9m) = 0.0948*(Tmin) - 321   for T in microseconds.

Appendix 2 - HRPD essential telephone numbers

To call a bleeper hit 70-bleeper number-5579 and wait for tone

If possible, please contact one of the instrument scientists before
calling an instrument support member at home.

Instrument Scientists:	phone	bleep	home phone
Bill David	5179	181	9-33153
Duncan Akporiaye	6420		
Adrian Barnes	5137		
Richard Ibberson	5871	206	9-34067
Chick Wilson	5137	203	9-08675-4206

Sample Environment:

Ken Quinton (general)	6182	173	9-7-65762
Mark Adams (furnace)	6502		
Ian Bailey (general)	5226	167	9-847304
Roger Bennett (general)	6379	152	9-0488-71718
Brian Boland (general operations)	5679	161	9-23171
Malcolm Page (cryostats)	5226	168	9-850390

Choppers:

Terry Jones (choppers)	6145	186	9-7-4258
Jack Parker(choppers/electronic)	5350		9-814733
Malcolm Fisher (" / ")	6647		9-22723

Computing:

Kevin Knowles (general)	5305	177	9-0635-49172
Bill Pulford (CAMAC/DAE)	6544	161	9-0993-850255
Steve Quinton (DAE/electronics)	5534	176	9-7-4552

Other useful numbers:

ISIS main control room	6789/6736
ISIS target station	6786
ISIS duty officer	6789/6736
ISIS radiation monitoring	6696
University liaison	5592/5103/6379

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Sample environment lab.	5226
Divisional administration	5115/6205/6615
Main gate/night transport	5545
Transport (daytime)	5317
Radiation protection	5430
Cosener's House	3007
Ridgeway House	72-2643
British Rail enquiries	9-0865-722333
Operator (daytime)	0
Outside line	9

EMERGENCY   2222