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GSAS

GENERAL STRUCTURE ANALYSIS SYSTEM

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GSAS Introduction....................1
GSAS Installation....................1
GSAS Organization....................7
- BIJCALC - Thermal Motion Analysis....................7
- CAD4RD - Input Enraf-Nonius Single Crystal Data....................7
- CLLCHG - Unit Cell Transformation Routine....................7
- DISAGL - Bond Distance and Angle Computation....................7
- EXPEDT - GSAS Editor....................7
- FITSPEC - Fitting of Incident Spectra....................8
- FORSRH - Fourier Peak Search....................8
- FORPLOT and PLOTTER - Fourier Map Display....................8
- FOURIER - Fourier Map Calculations....................8
- FPRIME - Calculate X-Ray Anomalous Dispersion Coefficients....................8
- GENLES - General Least Squares....................8
- GEOMETRY - Calculate Molecular Geometry....................9
- HKLSORT - Reflection Lister for Publication....................9
- HSTDMP - Powder Pattern Lister....................9
- ISTATS - Intensity Statistics....................9
- KUMARD - Input KUMA Single Crystal Data....................9
- ORTEP - Crystal Structure Plotting....................9
- P3R3DATA - Input Siemens P3R3 Single Crystal Data....................9
- POWPLOT - Powder Pattern Plotting....................10
- POWPREF - Powder Data Preparation....................10
- PROFTEST - Display of Powder Profile Shapes and Derivatives....................10
- PUBTABLES - Preparation of Tables for Publication....................10
- RAWPLOT - Plotting of Powder Patterns....................10
- RCALC - Analysis of Structure Factor Residuals....................10
- REFLIST - Reflection Data Lister....................11
- REFLTOASCII - Conversion Of Reflection File to ASCII....................11
- REFLTOBIN - Conversion of ASCII Reflection File to GSAS Binary....................11
- RDUCLL - Cell Reduction Routine....................11
- SCABS - Single Crystal Absorption Calculations....................11
- SCMERGE - Single Crystal Data Sort and Merge....................11
- SPCGROUP - Interpretation of Space Group Symbols....................11
- SXTLDATA - Generalized Input of Single Crystal Data....................11
- TDPLT - Drawing of Ball and Stick Models....................12
- UNIMOL - Assembling of Unique Molecules....................12
- Other Programs in GSAS....................12
- Utility Routines in GSAS....................12
- ATOM - Display of Atomic Scattering Factor Data....................12
- ELST, DLST, SLST, TLST - List File Utilities....................12
- PEXP, TEXP, DEXP, SEXP, LSEXP, EDEXP....................12
- EXPNAM, NEXT, SELECT, PREV - Experiment Selection Utilities....................13
- TLOG, DLOG - Log File Utilities (VMS only)....................13
- DBCH - Batch File Utility (VMS only)....................13

Program Execution in GSAS....................13
GSAS Program and File Layout....................14
Training Exercises - Introduction....................15
General Instructions....................16

Nickel Powder Example....17
  Introduction to EXPEDT....17
  Starting GSAS....17
  Running EXPEDT....18
Preparation of Powder Data - Program POWPREF....36
Plotting of Powder Data - Program POWPLOT....38
  Introduction....38
  Running POWPLOT....38
Setup for Least Squares - Program EXPEDT....44
  Introduction....44
  Running EXPEDT....44
Refinement of Powder Data - Program GENLES....53
Plotting of Results - Program POWPLOT....54
  Introduction....54
  Running POWPLOT....55
Suggestions for Further Work on 'NICKEL'....62
  Background Coefficients....63
  Zero....63
  Atom Parameters....63
  Profile Coefficients....63
  Other Parameters....63
Refinement of Yttrium Iron Garnet....65
  Powder Data Setup and Atom Data Entry....65
  Powder Data Preparation and Refinement....68
Fourier Setup and Calculations....71
  Fourier Map Display....76
Distance-Angle Setup and Calculations....80
Single Crystal X-ray Data Exercise....82
  CAD4 Data Setup....82
  Absorption Correction Setup and Calculations....92
  Intensity Statistics....95
  Data Merge and Patterson Calculations....97
  Map Search and Structure Solution....99
  Atom Insertion and Structure Refinement....100
  Anisotropic Refinement and Structure Results....104
  Structure Drawing....105
Mathematical Basis....115
  Introduction....115
  Structure Factors....115
  Total Powder Diffraction Profile Intensity....117
    Incident Intensity Function....118
    Background Functions....119
    Bragg Intensity - Yp,h....121
      Intensity Correction Factors....122
        Extinction in Powders....122
        Powder Absorption Factor....123
        Preferred Orientation of Powders....124
        Reflection Multiplicity....125
        Angle Dependent Corrections....125

- Profile Peak Shape Function 125
  - Neutron Time of Flight 126
  - Neutron and X-ray 2Q 126
- Profile Functions 127
  - TOF Profile Functions 127
  - Interpretation of TOF Powder Profile Coefficients 132
    - Strain broadening 132
    - Particle size broadening 133
  - CW Profile Functions 134
  - Interpretation of CW Powder Profile Coefficients 136
    - Strain broadening 136
    - Particle size broadening 137
- Reflection Peak Widths 138

Least Squares Theory 138

File Structures in GSAS 144
- Introduction 144
- File Name Conventions 144
- EXPNAM.EXP - The Experiment File 144
  - Overall data records 144
  - Crystal structure records 148
  - Histogram/phase records 152
  - Histogram records 154
    - All diffraction histogram types 154
    - Powder histogram records 155
    - Single crystal histogram records 158
    - SCD instrument histogram records 160
    - Soft constraint histogram records 163
  - Single crystal instrument data records 163
  - Constraint records 165
  - ORTEP records 166
  - Rigid body records 167
  - The last record 169
- Handling of EXPNAM.EXP File by GSAS 169
- EXPNAM.REFnnx - The Reflection Files 170
- EXPNAM.Phh - The Histogram Files 172
- EXPNAM.CMT - Variance-Covariance File 172
- EXPNAM.fmp - Fourier Map Files 173
- GSAS Standard Powder Data File 174
- ATOMDATA.DAT - Atom Data File 176
- Instrument Parameter File 177

GSAS Introduction

Welcome to the General Structure Analysis System (**GSAS**). **GSAS** is a set of programs for the processing and analysis of both single crystal and powder diffraction data obtained with x-rays or neutrons. It is capable of handling all of these types of data simultaneously for a given structural problem. In addition, it can handle powder diffraction data from a mixture of phases refining structural parameters for each phase. **GSAS** is designed to be easy to use and features a menu driven editor (**EXPEDT**) equipped with help listings and error trapping features. **EXPEDT** is used to prepare all input for the main calculation programs in **GSAS**. The entire **GSAS** system is written in FORTRAN and uses some system callable features. The current distributions of **GSAS** are available for both VMS and UNIX operating systems (VAX/VMS, Alpha/OpenVMS, Silicon Graphics Irix, DecStation Ultrix and Hewlett-Packard UX). An integral part of **GSAS** is the facility for interactive graphics display which is based on the Common Graphics System (CGS) of Los Alamos National Laboratory. **GSAS** supports many standard graphics terminals including X-windows work stations as well as Tektronix type terminals and DEC ReGIS terminals. It also supports various hard copy graphics devices (PostScript printers, DEC LA50 dot matrix printer, DEC laser printers, Hewlett-Packard printers and plotters, and CGS metafiles). This manual consists of three sections; this introduction, a training manual and a technical manual.

GSAS Installation

In this section we give the instructions for obtaining and installing a **GSAS** distribution kit for the DEC Alpha/OpenVMS and Silicon Graphics Irix (UNIX) operating systems from an anonymous ftp account at Los Alamos. Other distribution kits are available from the same source; detailed instructions are available in a file "readme.1st" located in the home directory of the anonymous ftp account. This manual is also available from this source in formats suitable for printing from both VMS and UNIX platforms on Postscript printers.

An Anonymous FTP Server for **GSAS** on DEC Alpha/OpenVMS Codes

The **GSAS** distribution kit for DEC Alpha/OpenVMS contains two large files which are kept in a compressed form that is approximately 50% smaller than the original. Also stored in this directory are the executable forms of the programs for compression and decompression of any file. These files need to be transferred in binary format. There are also two smaller command files and a document file describing the compression routines along with this "readme" file. These latter files are transferred in ASCII format.

GSAS Installation from ftp files:

System Requirements: Alpha/OpenVMS Version 1.5 or later,
SYS$LIBRARY:DECW$XLIBSHR must be an installed image.

To ensure that the file structure and command files for **GSAS** are set up appropriately on your Alpha, we have provided an installation procedure and a command file. These instructions cover both the initial installation of **GSAS** on an Alpha as well as the replacement of an old version of the system. If there is an existing **GSAS** to be replaced the first step is omitted and the entire directory structure for **GSAS** will be replaced. Thus it is not advisable to use any of the **GSAS** directories for any other files. This installation scheme is used if you obtain the installation files by ftp file transfer from Los Alamos.

1. Set up a subdirectory named [.GSAS] or a main directory [GSAS]. Sufficient disk space to hold the system should be made available (ca. 25000 blocks).

2. Set the current directory to the directory created in step 1 (e.g. SET DEF [GSAS]).

3. Initiate contact with the distribution machine at Los Alamos:

```
ftp mist.lansce.lanl.gov
```

This is a DEC Alpha/OpenVMS machine. When you get a MIST.LANSCE.LANL.GOV> prompt, type:

```
login anonymous
```

When you get the prompt for a password, type your e-mail address. To get general information concerning the files, type (but not the stuff in parentheses)

```
ASCII              (to set the mode of transfer)
get readme.1st     (to transfer the file)
cd [.alphavms]     (to change to the alpha distribution directory)
get alphagsas.ftp  (to transfer this readme file)
```

These files should be read off-line; they contains general information about the versions of **GSAS** that are currently available as well as this instruction file. If you wish to obtain a new version of **GSAS** for DEC Alpha/OpenVMS, type the following commands:

```
binary             (set the mode of transfer)
mget *.lz          (transfer the compressed files)
```

If the decompression routines are not already available, type:

```
mget lz*.exe       (transfer lzcmp.exe and lzdcmp.exe)
```

which transfers the compression and decompression utilities. The executables were linked under OpenVMS V1.5 and should run on all Alpha/OpenVMS systems. To complete the file transfer, type:

```
ASCII              (set the mode of transfer)
mget *.com         (transfer the files)
mget *.doc
quit               (exit ftp)
```

The file, IMPORT.COM, is the installation routine for **GSAS**. It will process the other files and produce a working version of **GSAS** on your machine. Details of its operation are given below. The file, LZSOURCE.COM, is a self-unpacking archive file. If you desire source code for the compression routines and you have a C compiler, then issue an @SOURCELZ command, followed by an @LZBUILD command to create the new compression executables. LZCOMP.DOC is documentation for the compression utilities.

4. Run the import command file. (e.g. @IMPORT). After this completes you are in the subdirectory [GSAS.COM].

While running IMPORT.COM you will be asked about the names of batch queues. **GSAS** requires that your Alpha have at least one batch queue and will support up to three queues. You can use the default of SYS$BATCH but a better sharing of resources can be obtained with queues for fast, medium and slow jobs. If the queues are not yet determined you can change them later by editing the file [GSAS.COM]GSASDEF.COM and inserting the queue names. The command file asks four questions to determine the portions of **GSAS** you desire and will submit up to 36 batch jobs to SYS$BATCH. (Currently none of the LANSCE specific parts of **GSAS** are operational on Alpha/VMS.) In this way the executable versions of the **GSAS** programs are created for your version of the VMS operating system. After these batch jobs complete, you may wish to free ca. 10000 blocks of disk space by deleting the libraries which are contained in the directory [GSAS.LIB]. Before the command file finishes it will inform you of the symbol definition for **GSAS** that should be placed in either a system wide login file or else each user login file.

An Anonymous FTP Server for **GSAS** SGI Irix Codes

The **GSAS** distribution kit for Silicon Graphics Irix contains a single large file which is kept in a compressed form that is approximately 50% smaller than the original. This file needs to be transferred in binary format. There is also this "readme" file which is transferred in ASCII format.

GSAS Installation from ftp files:

System Requirements: SGI Irix 4.x or 5.x with f77 and XWindows. For Irix 5.x, an additional file will need to be transferred which contains the executables.

To ensure that the file structure and command files for **GSAS** are set up appropriately on your SGI we have provided below an installation procedure and an "install" script file. This installation scheme is used if you obtain the installation files by ftp file transfer from Los Alamos.

1. Set up a directory named "gsas" in a convenient location on your file system. (e.g. "mkdir ./gsas"). Note that sufficient disk space (ca. 50Mb) to hold the all the **GSAS** files is needed in the file system.

2. Set the current directory to the directory created in step 1 (e.g. type "cd ./gsas"). Make a note of the full name of this directory (e.g. type "pwd"); you will need this name for step 4, below.

3. Initiate contact with the distribution machine at Los Alamos:

```
ftp mist.lansce.lanl.gov
```

(This is a DEC Alpha/OpenVMS machine.)

When you get a prompt for "Name", login as:

```
anonymous
```

(If you get an ftp> prompt, type "user anonymous"). When you are prompted for a password, type your e-mail address.

To get general information concerning the files, type the following (without the stuff in parentheses).

```
ASCII                   (to set the mode of transfer)
get readme.1st          (to transfer the file)
cd [.sgiunix]           (to change to the SGI distribution directory)
get sgigsas.ftp         (to transfer this readme file)
```

(Read these files off-line; they contain general information about the versions of **GSAS** that are currently available as well as this instruction file. To obtain a new version of **GSAS** for your SGI, type the following commands:)

```
binary                  (set the mode of transfer)
get GSAS.TARZ           (transfer the compressed file)
```

If you are running Irix 5.x, you will need to transfer the following:

```
get GSASEXE.TARZ        (transfer the compressed file of executables)
```

Then exit ftp by

```
quit                    (exit ftp)
```

Next rename the file GSAS.TARZ and GSASEXE.TARZ files so that the decompression routine will properly convert it, decompress it to create file gsas.tar and then restore the **GSAS** files. Use the following commands to do this:

```
mv GSAS.TARZ gsas.tar.Z   (rename the compressed file)
mv GSASEXE.TARZ gsasexe.tar.Z  (if necessary)
uncompress gsas.tar       (creates gsas.tar from gsas.tar.Z)
uncompress gsasexe.tar    (if necessary)
tar -xvf gsas.tar         (creates all the gsas files)
tar -xvf gsasexe.tar      (creates the executables for Irix 5.x)
```

You may now delete gsas.tar to save ~13Mb of disk space.

```
rm gsas.tar             (delete file)
```

The script file, "install", completes the installation for **GSAS** on Irix 4.x; it is not needed on Irix 5.x. It uses the f77 command to load the executables for **GSAS** from all the object files it finds in ./gsas/gsasmain and puts the .exe files into the directory ./gsas/exe. After it finishes you may delete the files libgsas.a and the contents of ./gsas/gsasmain to save ~6Mb of disk space. The commands are:

```
install                 (load the gsas executables)
rm libgsas.a            (delete the library)
rm gsasmain/*           (delete the object files)
```

4. Finally you need to edit your .cshrc file to include an alias like

```
alias gsas /usr/gsas/gsas
```

to point at the path for the script file gsas (replace "/usr/gsas" with the location you chose for gsas (see step 2).

You are now ready to use **GSAS**. Everything that is in the present **GSAS** manual will work as in the VMS versions except that UNIX style file paths must be used for the exercises. For example, use "/usr/gsas/gsas_exercises/NICKEL.RAW" for the data set name in the first exercise. (Your path will be different depending on where you put the directory gsas.)

If there are any problems or questions call:

Bob Von Dreele (505)-667-3630 e-mail: VONDREELE@LANL.GOV
Allen Larson (505)-667-2942 e-mail: ALARSON@LANL.GOV

GSAS Problem Reporting

If you experience any difficulties with the operation of **GSAS**, find any errors or want to suggest any changes please use the form found on the next page for reporting them.

Submit to: GSAS Manager, Los Alamos National Laboratory, LANSCE, MS H805, Los Alamos, NM 87545 USA

GSAS Problem Report

Title:		ID: Date:
Module name:	Link date:	Problem type ( ) Software ( ) Documentation ( ) Other

Problem Description:

Enclosures (documenting hardware/software context of the problem):

[ ] On-line listings [ ] Off-line listings

Date problem was first noticed:	Were you able to recover?	Is the problem repeatable?

DO NOT WRITE BELOW THIS LINE

Remarks/Analysis:

ACTION	BY	DATE
Received		
Analyzed		
Acted on		
Notified		

GSAS Organization

GSAS is organized into several main programs each designed for specific types of tasks or types of crystallographic calculations. They are listed below in alphabetic order with a brief description of their features. The various **GSAS** specific files generated by these programs are given in single quotes; they are described in the technical section of this manual. All of these programs as well as a number of utility routines are accessed through the **GSAS** shell which is invoked by entering **'GSAS'** on your terminal. This shell is capable of filtering the **GSAS** commands from other VMS/UNIX commands so that all terminal operations can be done from within the shell. In other words, you are able to do virtually any VMS or UNIX command from within the **GSAS** shell.

BIJCALC - Thermal Motion Analysis

BIJCALC is an interactive routine that analyzes the anisotropic thermal motion parameters and prints some information derived from the values on the list file.

CAD4RD - Input Enraf-Nonius Single Crystal Data

CAD4RD is an interactive routine for reading data measured on the Enraf-Nonius CAD4 instrument, extracting the unit cell information, examining the standard reflections and writing the reflection data into the 'reflection file' with corrections for crystal decay, etc. as indicated by the standard reflections. It also copies the ψ scan data into the 'experiment file' for use in absorption correction calculations.

CLLCHG - Unit Cell Transformation Routine

CLLCHG is an interactive routine for transforming a unit cell and its contents to a different description associated with a, for example, second order phase transition.

DISAGL - Bond Distance and Angle Computation

DISAGL is a batch program to calculate interatomic distances and angles. By using the variance-covariance matrix it also determines estimated standard deviations for these values.

EXPEDT - GSAS Editor

EXPEDT is the interactive editor for **GSAS.** It is generally the first program in **GSAS** run by the user. All input of structural data, program controls and other non-diffraction data is handled interactively by **EXPEDT**. Program control within **EXPEDT** is from a nested series of menus. The choices in the first layer of menus determine what kind of calculation is to be setup; choices in each succeeding menu layer determine finer detail in the setup. Each menu has a help listing associated with it which can be displayed as one of the menu options, thus **EXPEDT** is largely self documenting. **EXPEDT** also has graphics facilities for displaying powder patterns on a graphics terminal to facilitate editing of certain parameters. The second section of this manual contains training exercises which take you through the sequence of steps for running **EXPEDT** during the course of some crystallographic problems. **EXPEDT** modifies the experiment specific control file as the user makes menu selections and inputs data. In **GSAS** this file is known as the 'experiment file' and has the name 'somename.EXP'. It is fully described in the technical section of this manual. During the operation of **EXPEDT** an updated version of the experiment file is created which then becomes the input for any succeeding program in **GSAS**. In the case of VMS systems multiple versions are retained (depending on how "VERSION_LIMIT" is set on your machine). For UNIX systems only one previous version is retained; it has the name 'somename.OLD'.

FITSPEC - Fitting of Incident Spectra

FITSPEC is an interactive routine used to fit the incident spectra from a particular instrument to a variety of functions. It is generally needed only for TOF neutron data. The results are output to an 'instrument parameter file'.

FORSRH - Fourier Peak Search

FORSRH is an interactive Fourier peak search routine. It lists the positions and heights of the peaks found on the 'Fourier map file' and places them in the 'experiment file' for inclusion in distance and angle calculations.

FORPLOT and PLOTTER - Fourier Map Display

FORPLOT and **PLOTTER** are two interactive Fourier map display programs. They are capable of producing on various graphics devices (same as those supported by **EXPEDT**) single map slices, stereo views or interpolated oblique slices of maps generated by **FOURIER** and stored on 'Fourier map files'.

FOURIER - Fourier Map Calculations

FOURIER is a batch oriented standard Fourier map generation program. It can produce xy, xz or yz sections of Patterson, F_O, F_C or ΔF maps. The output is mainly a 'Fourier map file' intended for input to the peak search routine, **FORSRH**, and the graphics display programs, **PLOTTER** and **FORPLOT**. As an option it will produce a numerical map in the list file.

FPRIME - Calculate X-Ray Anomalous Dispersion Coefficients

FPRIME is a modified version of the program written by D. T. Cromer (Acta Cryst. 18,17-23, 1965) which calculates the X-ray anomalous dispersion coefficients and absorption coefficient for any energy. This interactive program will perform these calculations for up to seven energies or wavelengths for a single element using one of three possible methods (method 2 is recommended). It reads the tables of atomic cross sections from the file [GSAS.PARM]XSECT.NDAT. It operates independently of the **GSAS** file structure.

GENLES - General Least Squares

GENLES is a batch oriented least squares refinement program derived in part from a program by the same name written by Allen C. Larson. It constructs a single full least squares matrix and vector using multiple data sets. A mixture of powder diffraction and single crystal data for a given structural problem can thus be processed simultaneously. It also has facilities for constructing linear constraints between parameters, rigid body constraints for molecular fragments and can include bond length observations as 'soft constraints'. **GENLES** outputs a summary of the least squares results on a list file and generates an updated version of the 'experiment file'.

GEOMETRY - Calculate Molecular Geometry

GEOMETRY is an interactive program which will produce on the list file and on the terminal the results of several kinds of molecular geometry calculations. These include the orientation and position of a selected string of atoms as a rigid body, application of thermal motion corrections to selected bonds, hydrogen atom generation from carbon atom positions and calculation of specific torsion angles.

HKLSORT - Reflection Lister for Publication

HKLSORT is an interactive program which will produce on the list file a sorted list of structure factors in a form suitable for deposit with a journal. This list can be structured to have any one of the indices *hkl* as the fast running index and another as the slow running index. Thus, all six cases of *hkl* tables are permitted.

HSTDMP - Powder Pattern Lister

HSTDMP is a powder pattern data listing program. It can list interactively sections of a 'histogram file' or produce a list file of the entire powder pattern in a form suitable for deposit with a journal.

ISTATS - Intensity Statistics

ISTATS is an interactive program used to help determine the space group by creating a list of the average value of $F^2/\sigma(F^2)$ for the various parity classes of reflection sets such as *h00, hk0*, etc.

KUMARD - Input KUMA Single Crystal Data

KUMARD is an interactive routine for reading data measured on the KUMA single crystal instrument, extracting the unit cell information, examining the standard reflections and writing the reflection data into the 'reflection file' with corrections for crystal decay, etc. as indicated by the standard reflections. It also copies the ψ scan data into the 'experiment file' for use in absorption correction calculations.

ORTEP - Crystal Structure Plotting

ORTEP, written by Carroll Johnson (ORNL Report 5138), has been modified to adhere to the **GSAS** style with menus and interactive graphics. The current version implements most of the original ORTEP-II instructions through menu responses.

P3R3DATA - Input Siemens P3R3 Single Crystal Data

P3R3DATA is an interactive routine for reading data measured on the Siemens P3R3 single crystal instrument, extracting the unit cell information, examining the standard reflections and writing the reflection data into the 'reflection file' with corrections for crystal decay, etc. as indicated by the standard reflections. It also copies the ψ scan data into the 'experiment file' for use in absorption correction calculations.

POWPLOT - Powder Pattern Plotting

POWPLOT is an interactive graphics program for displaying powder diffraction patterns on various graphics devices. It is capable of displaying observed, calculated and difference curves with reflection markers at the user's option. It can also analyze the weighted differences and produce normal probability plots. In order to use **POWPLOT** on a particular powder pattern, **POWPREF** must have been run at least once. This program also has the ability to calculate the Fourier transform of the residuals to determine the radial distribution function of an amorphous phase, if one is present.

POWPREF - Powder Data Preparation

POWPREF prepares powder diffraction data for subsequent least squares analysis. The major tasks of **POWPREF** are to associate the position, channel or step width, incident intensity, refinement weight and a list of contributing reflections with each observation in a powder pattern. Additional flags are set for excluded regions, reflection markers, etc. for each point. Thus, **POWPREF** generates the full list of unique reflections from the lattice parameters and space group information for each phase in the sample; systematic extinctions and reflection multiplicities are automatically determined. There is a set of reflections generated for each powder pattern in the data set. **POWPREF** outputs a brief summary of its work on a list file and produces a 'reflection file' and a 'histogram file' for each powder data set processed.

PROFTEST - Display of Powder Profile Shapes and Derivatives

PROFTEST displays individual computed powder profile shapes for any of the profile functions available in **GSAS**. The profile shapes may be varied by adjustment of the profile coefficients and peak position (2Θ or TOF). Numerical and analytic derivatives of the profiles with respect to profile coefficients may also be displayed. It operates independently of the **GSAS** file structure and is generally used for diagnostic purposes.

PUBTABLES - Preparation of Tables for Publication

PUBTABLES prepares tables of structure factors and atomic parameters which are suitable for publication purposes.

RAWPLOT - Plotting of Powder Patterns

RAWPLOT is a graphics routine for displaying powder diffraction data in either d-spacing or data collection units (2Θ or time-of-flight). The input data must be in the **GSAS** standard raw data file format and an 'instrument file' is also required.

RCALC - Analysis of Structure Factor Residuals

RCALC is an interactive program which can be used to determine R-indices for the various parity classes of reflections. It also can be used to generate plots of residuals vs. a number of data parameters, such as d^*, F_{obs}^2, etc.

REFLIST - Reflection Data Lister

REFLIST is a reflection listing routine. It is capable of listing on either the terminal screen or on the listing file some or all of the reflections associated with each histogram.

REFLTOASCII - Conversion Of Reflection File to ASCII

REFLTOASCII converts **GSAS** reflection files (single crystal or powder) into an ASCII form suitable for transfer between VMS and UNIX machines. The ASCII files may also be read by nonGSAS crystallographic software (e.g. MULTAN). (See REFLTOBIN below).

REFLTOBIN - Conversion of ASCII Reflection File to GSAS Binary

REFLTOBIN converts ASCII files created by **REFLTOASCII** back to **GSAS** reflection file format.

RDUCLL - Cell Reduction Routine

RDUCLL is a unit cell reduction routine originally written by Yvon LaPage. It finds the conventional representation of the cell and detects any possible pseudosymmetry. It operates independently of the **GSAS** file structure.

SCABS - Single Crystal Absorption Calculations

SCABS is a batch oriented program for making absorption corrections to single crystal data from either X-ray or neutron single crystal instruments.

SCMERGE - Single Crystal Data Sort and Merge

SCMERGE is a batch oriented program for merging single crystal reflection data into a unique set with standardized reflection indices which are written to a new 'reflection file'. The space group extinct reflections are omitted and the Friedel related reflections are flagged and written adjacent to the standard reflection in the output 'reflection file'.

SPCGROUP - Interpretation of Space Group Symbols

The interactive program **SPCGROUP** interprets space group symbols to give a table of the equivalent positions and will do this for any setting of the 230 three dimensional groups except that trigonal, rhombahedral, tetragonal and hexagonal space groups must have the c-axis as the unique axis. Optionally it will determine the site symmetry rules for any location in the unit cell. It will also process spin flip assignments for magnetic symmetry and display a stereo pair drawing showing the resulting pattern of magnetic moments. The routines in **SPCGROUP** are those used elsewhere in **GSAS** for space group symbol interpretation.

SXTLDATA - Generalized Input of Single Crystal Data

SXTLDATA is a generalized structure factor input routine for single crystal data from an ASCII file which is then put into a standard **GSAS** format reflection file.

TDPLT - Drawing of Ball and Stick Models

TDPLT is an interactive program for generating views of the crystal structure. Several options are available for determining the space included in the drawing, namely, a sphere about a point in the unit cell, rectilinear blocks of space, and parallelogram blocks terminated by unit cell edges. Thermal ellipsoids are represented by plotting only the principal ellipses. Bonds are represented only by lines, but can have the bond length plotted in the center of the bond. Two classes of bonds are represented as either solid lines or dotted lines. There is no hidden line elimination.

UNIMOL - Assembling of Unique Molecules

UNIMOL is an interactive program for assembling unique molecules from the atoms in the 'experiment file'. The current version is rather crude in that it does nothing to maintain the continuity of a string of atoms, but only insures that all atoms in the molecule are in a contiguous set in the 'experiment file'. One however has the option of rearranging the atom list to suit their needs.

Other Programs in GSAS

In addition to the 36 programs listed above there are an additional 20 which are specific to crystallographic data processing at LANSCE which are only available for the VAX/VMS version of **GSAS**. They include routines for display of LANSCE data, preliminary data reduction, pole figure analysis from SCD data and various other routines.

Utility Routines in GSAS

There are a number of utility routines in **GSAS** that simplify many routine operations with **GSAS** list files, etc. as well as provide easy access to some of the data files within **GSAS**.

ATOM - Display of Atomic Scattering Factor Data

The **ATOM** facility displays for the selected chemical element (e.g. ATOM TI) all the information stored on the file ATOMDATA.DAT for that element.

ELST, DLST, SLST, TLST - List File Utilities

ELST is for editing the list file using the system standard editor; **DLST** is used to delete the list file, **SLST** is used to search the list file for a string and **TLST** will display the list file on the terminal.

PEXP, TEXP, DEXP, SEXP, LSEXP, EDEXP - Experiment File Utilities

PEXP (VMS only) is used to purge the experiment files, **TEXP** is used to list the experiment file on the terminal, **DEXP** (UNIX only) is used to delete all files for the experiment except the experiment and raw data files, **SEXP** is used to search the experiment file for a string, **LSEXP** (UNIX only) is used to list the names of all experiment files in the directory, and **EDEXP** is used for editing by hand (not recommended) the experiment file.

EXPNAM, NEXT, SELECT, PREV - Experiment Selection Utilities

EXPNAM is used to set a particular experiment name to be used for subsequent **GSAS** operations. **NEXT** and **PREV** (UNIX only) select the next (or previous) experiment in alphabetical order. **SELECT** (VMS only) lists the available experiments in the directory and prompts for your selection.

TLOG, DLOG - Log File Utilities (VMS only)

TLOG displays the log files for the current experiment on the terminal; **DLOG** deletes these log files.

DBCH - Batch File Utility (VMS only)

DBCH is used to delete batch files. This utility is most commonly used when a batch job fails with a system error leaving a number of uncompleted batch files in the directory which must be deleted before **GSAS** will allow further work on that experiment.

Program Execution in GSAS

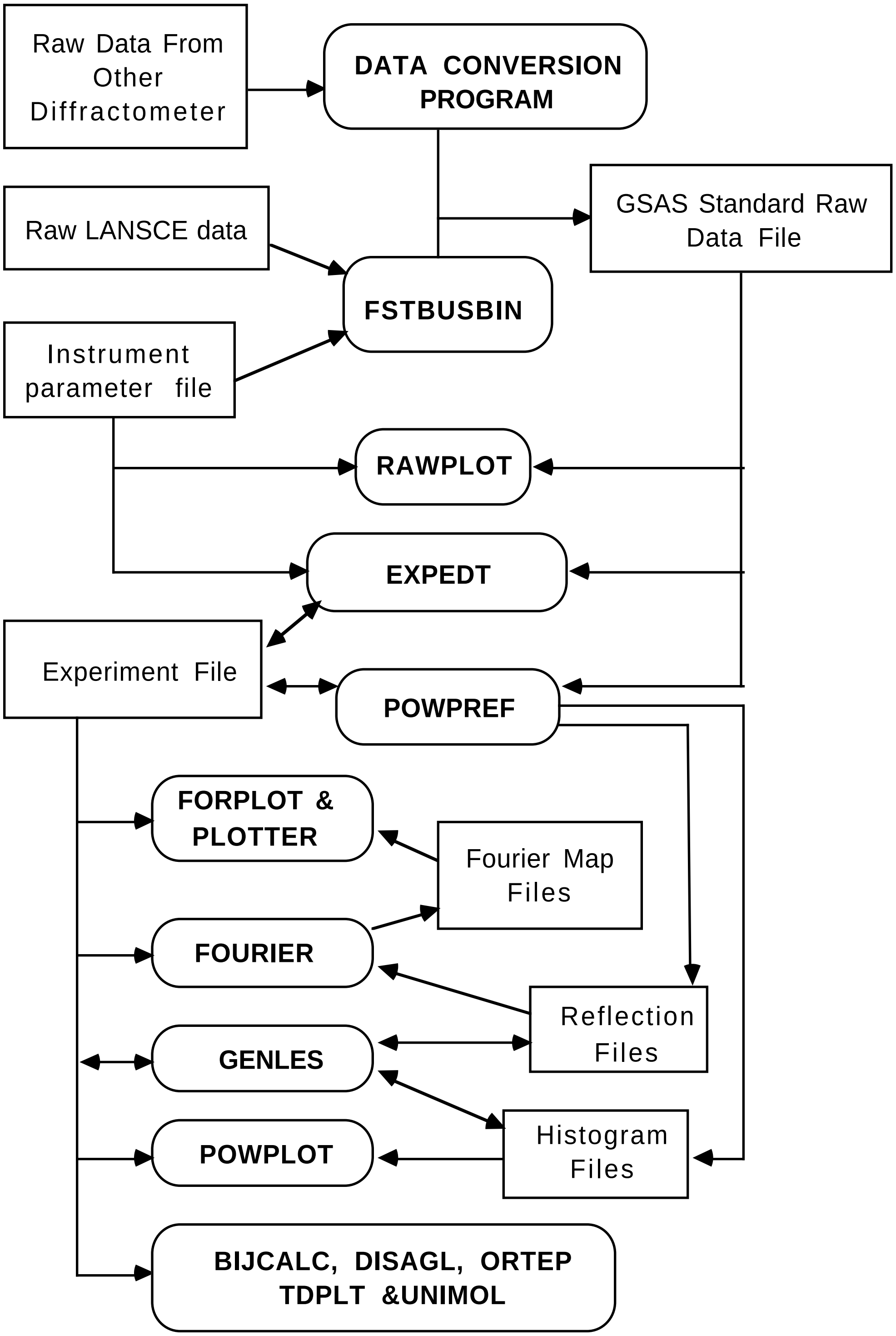
The programs in **GSAS** are either executed in interactive mode (e.g. **EXPEDT**) or optionally in batch mode (e.g. **GENLES**). For each program request in **GSAS** the shell will determine whether it is interactive or possibly batch.

For **GSAS** on VMS systems, the shell will examine the command line looking for additional batch routines to be set up as a sequence. For example the command line **'POWPREF GENLES FOURIER FORSRCH DISAGL'** will cause the five batch routines to be executed in sequence as separate jobs. For each one the shell will request from you the appropriate batch queue and instructions for handling the log file and then produce a "batch" file. The batch files are named 'EXPNAME$PGMNAME.BCH'. The first one is submitted to the requested queue; as it finishes it submits the next one to be executed and then deletes itself. If a program aborts with an error the remaining routines are not executed and the remaining batch files will still exist in your current directory. They will have to be deleted before any **GSAS** routine can be run on the experiment (use the utility **DBCH** to remove them).

On UNIX systems, all the programs in **GSAS** are assumed to be run interactively although **POWPREF**, **GENLES** and some others may optionally be run in the background. Unlike VMS, input of multiple programs on one command line is not allowed and will generate an error.

GSAS Program and File Layout

The layout of the programs in **GSAS** and the interconnecting files for powder calculations is shown in the following figure. The program names, which are not inclusive, are shown in boldface; the arrows indicate the direction of input and/or output by each program.



Training Exercises - Introduction

This training manual consists of three exercises which introduce you to **GSAS**. The first exercise is designed for the user who has never used **GSAS** and covers only those facilities needed to do a Rietveld refinement from time of flight (TOF) neutron powder data. The second exercise is for the more experienced user and is based on a Rietveld refinement with constant wavelength (CW) neutron powder data and includes instruction for using some additional features of **GSAS**. The third exercise covers the input, structure solution and refinement from a single crystal x-ray diffraction data set.

The first exercise takes you through the sequence of steps needed to refine the variables in a diffraction experiment on nickel powder using data taken on a TOF powder diffractometer at the Manuel Lujan, Jr. Neutron Scattering Center (LANSCE), Los Alamos National Laboratory. The first step in this exercise is to give some minimal structural information (space group and lattice parameters) and bring the experimental powder patterns into **GSAS** using program **EXPEDT**. After this initial step, you will run the batch process **POWPREF**, which takes this information and prepares the powder histograms for structure refinement by generating the set of reflections covered by the powder pattern and matching them against the powder patterns. After **POWPREF** completes you will examine its results using the powder pattern graphics program **POWPLOT**. Then a second session with **EXPEDT** will complete the editing process by introducing the remaining structural information (atom positions, etc.) and setting suitable refinement controls for refinement by **GENLES**. The newly calculated powder patterns are then examined with **POWPLOT**. At the end of the exercise there are suggestions for additional least squares calculations.

The second exercise describes the refinement of a yttrium-iron garnet using CW neutron data taken on the D1a powder diffractometer at the Institut Laue-Langevin, Grenoble, France. The first steps follow the same pattern as the first exercise. After the refinement is complete there is described the calculation and display of Fourier maps using **FOURIER** and **FORPLOT** and calculation of interatomic distances and angles with **DISAGL**.

The third exercise begins with the input of a single crystal x-ray data set of oxonium hexafloroantimonate collected on an Enraf-Nonius CAD4 diffractometer using the program **CAD4RD**, followed by the preliminary data processing steps of absorption corrections (**SCABS**), sorting and a merge of the data (**SCMERGE**) to give the unique reflection set. This is followed by calculation of a Patterson with **FOURIER** which is searched for peaks with **FORSRH**. After you interpret the Patterson, the rough atomic coordinates are subjected to least squares refinement. After some final refinement steps, the interatomic distances and angles are calculated with **DISAGL** and the structure is drawn with **ORTEP**.

To use this training guide most effectively, you should run the **GSAS** system responding to the program prompts as shown in this manual sequentially following the three exercises. Plan on taking 10-30 minutes for each session with **EXPEDT**, **POWPLOT** and **FORPLOT**. The turnaround times for batch runs of **POWPREF**, **GENLES**, **FOURIER** and **DISAGL** will depend on the loading and speed of your particular system and will be in the range of a few seconds to several minutes (possibly more). All operations with **GSAS** on a given problem must take place in the same directory, thus you should begin the training exercise in a directory where you will be able to continue work on the problem. Do not use any of the **GSAS** directories for the exercises.

General Instructions

Many of the prompts from the interactive programs in **GSAS** consist of a short description followed by a string of possible one-letter instructions. For example:

```
Enter command (<?>,D,I,L,M,P,T,X) >
```

The appropriate response is to type one of the possible letters followed by a carriage return **'CR'**. Note: this guide will show all possible user input bolded in single quotation marks; the quote marks are <u>NOT</u> to be input. The response given in angle brackets (<>) is the default; if only a **'CR'** is given that response is assumed by the program. In most cases the default response generates a help listing; these are indicated by <?>. In many cases one of a simple yes/no response is the default. Some of these one letter responses may lead to additional entries; they can usually be given on the same line or, if not, the program will prompt with the appropriate request. In any case all input lines must be terminated with a carriage return **'CR'**; at that time the commands will be executed.

Some program prompts require the entry of lists of various items; these can either be given all on a single line or on different lines. If the latter mode is chosen, the program will prompt for the remaining entries. Similarly, if a typographical error is made so that a value is not interpretable, the program will accept the values preceding the one in error, print an error message and then prompt for the value in error and any remaining values. In some cases the program will have a set of default values available for the requested items. These can be selected by simply typing **'/'** and the defaults for those items will be used. Otherwise you can enter a series of commas as place markers, the new value you wish to change, and a **'/'** to accept the remaining defaults. The items in any input list must be separated by either spaces, tabs or left justified commas.

Decimal values may be entered as either floating point values with a decimal point, scientific form with mantissa and exponent or integer fraction (e.g. 120.0, 1.2e2 or 2400/20 all equal 120.0). In a few cases the program will request text input; these inputs can consist of any ASCII characters. Text input for titles are limited to 66 characters, atom types and atom names are limited to eight characters, and space group symbols are limited to 20 characters. The character cases are retained for titles and atom names, and the character cases for the space group symbols are converted to conform with standard usage. Otherwise, the case of the input characters is immaterial.

As you begin to remember more of the arrangement of the menus in **GSAS**, you may know in advance the sequence of commands needed to setup some calculation. In general the system will accept a string of commands and numbers all on a single line separated by spaces even though the commands may involve several switches of menus. The system will generally stop such a sequence only where a pause is necessary to prevent a possible serious error or when an uninterpretable command or illegal numeric value was given. For example, forced pauses occur before atoms can be deleted and after a plot is displayed. There are other similar places where forced pauses occur. If a command in a long string can not be interpreted, **GSAS** will usually print a menu help listing at the point of error and the remaining commands on the string are ignored. This 'type ahead' feature of **GSAS** allows the expert user to quickly move to a particular menu or option, make the needed change and exit the particular routine without seeing a lot of intermediate questions or menus.

VMS and UNIX File Names in GSAS

In these exercises as well as during normal use of **GSAS** you are occasionally asked by the system to input a file name. Typically this file is a "raw" data set or an instrument parameter file. VMS and UNIX use very different constructions for directory and file names. In VMS a file name is of the form 'DISK:[NAME1.NAME2]FILE.EXT' while for UNIX the structure is more like '/name1/name2/file.ext' (notice that there is no disk name). VMS file names are insensitive to case; they always appear as upper case but either case can be used to name them. On the other hand UNIX file names are case sensitive, i.e. 'structure.dat' is a different file name from 'Structure.dat', so one must exercise care in entering UNIX file names in **GSAS**. In the examples below, we will show the VMS file name as appropriate and the equivalent UNIX name in parentheses. The UNIX path name, i.e. the /name1/name2/ part, for the examples depends on the location of **GSAS**. We will assume that it is installed as /usr/gsas. If you have installed it elsewhere you will have to modify the path names in these examples as you work them.

Nickel Powder Example

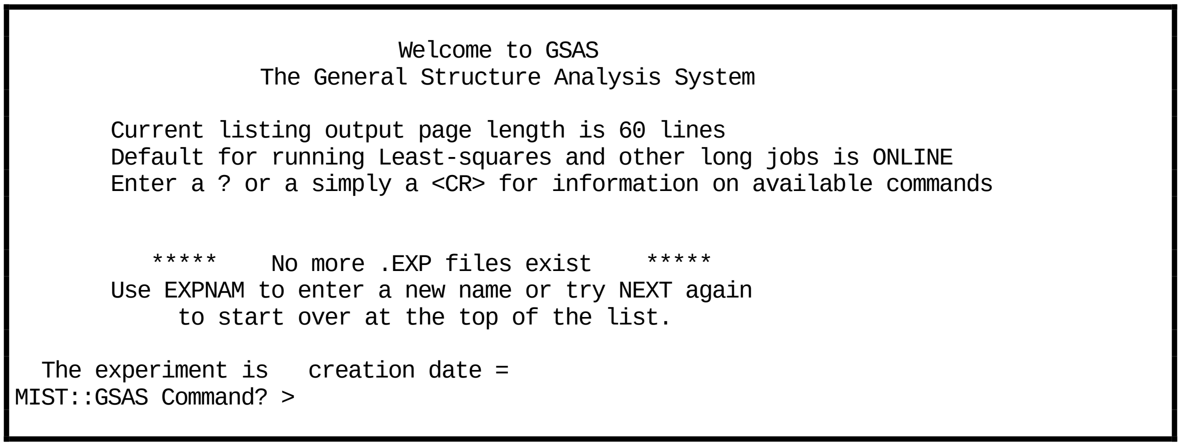
This section of the training manual covers the initial loading of powder diffraction data for the first example problem. This example problem consists of two powder patterns for nickel which will be subject to simultaneous Rietveld refinement.

Introduction to EXPEDT

EXPEDT is the main program for entry of all controls, data and commands for the processing of diffraction data by **GSAS**. It is a multilayer menu driven interactive editor and is capable of monitoring input for crystallographic as well as typographical errors.

Starting GSAS

The **GSAS** system is initialized by simply typing **'GSAS'** after the system prompt. The following opening screen for **GSAS** is then displayed on your terminal. Note: the pictured displays on your terminal may not exactly match those shown in this manual. The opening screen for the UNIX version is different but conveys the same information.



```
                          Welcome to GSAS
                The General Structure Analysis System

       Current listing output page length is 60 lines
       Default for running Least-squares and other long jobs is ONLINE
       Enter a ? or a simply a <CR> for information on available commands


          *****    No more .EXP files exist    *****
       Use EXPNAM to enter a new name or try NEXT again
            to start over at the top of the list.

  The experiment is   creation date =
MIST::GSAS Command? >
```

The message in the center of the screen results because **GSAS** fails to find an experiment file in your directory; normally it defines the first one alphabetically as the default experiment. Notice that the command line may also give the 'node name' for the particular computer you are working on. To display the main menu of components of **GSAS** type **'?'** or **'CR'**. For UNIX systems, type **'help'**.

```
The available commands are
ATOM          List atom scattering data for an element
EXPNAM        Enter a new experiment name
NEXT          Search for a new experiment to work on
SEL*ECT               List experiments available and select from the list
PAGE          Set the page length for the listing file
ONLINE        Set the default for GENLES, POWPREF, etc. to ONLINE
OFFLINE               Set the default for GENLES, POWPREF, etc. to OFFLINE
DEFAULTS      Display current default settings for PAGE and ON/OFFLINE

Additional information is available from the commands
GENERAL               List the general crystallographic commands
POWDER        List the powder data only commands
SINGLE        List the single crystal only commands
LANSCE        List the LANSCE specific commands
UTILITIES     List the GSAS utility routines

EX*IT,QU*IT   Exit from the GSAS command file

Control-Y is trapped and always returns you to the command request line

  The experiment is   creation date =
MIST::GSAS Command? >expnam nickel
```

This listing includes general purpose routines (**ATOM** etc.) and references to sublistings of routines specific to certain parts of a crystal structure analysis. Enter some of these and see what is listed for each. All of the programs are started from this menu. First you have to establish an experiment name for this training exercise; this name becomes the common file name for all files generated by **GSAS** programs. Enter **'EXPNAM NICKEL'** to set the experiment name. **GSAS** will then prompt for a new command.

```
%SYSTEM-W-NOSUCHFILE, no such file
 \NICKEL.EXP\
  The experiment is NICKEL  creation date =
MIST::GSAS Command? >
```

Running EXPEDT

The system warning message and the lack of a creation date indicates that the experiment file does not yet exist in this directory; in a moment you will create one. You are now ready for your first editing session; type **'EXPEDT'** to initiate the program. The program will display a question concerning your experiment.

```
Experiment - NICKEL - was not found.
Do you wish to create it (Y/<N>)? >
```

The message on the above screen tells you that the experiment file NICKEL.EXP does not exist in the current directory. Since you are starting on a new problem type **'Y'** so that the file will be created. If, after having created an experiment file, you get this message when you start **EXPEDT** it means that either you are not in the proper directory or else you misspelled the experiment name. In both cases simply type **'CR'**, the program will exit and then you should either change to the proper directory or change the experiment name as appropriate and try again. A third possibility is that your experiment file has been deleted. If this is the case, you are basically out of luck unless there is a copy or a backup of your experiment file; otherwise you must start from scratch and recreate a new experiment file. The new lines tell you the experiment file was created and gives you a new prompt.

```
The new experiment - NICKEL - has been created.
 Enter a title for this experiment
  >
```

The program is now requesting a text string up to 66 characters in length. This title will appear on various output listings and will be part of the initial display from **EXPEDT** and **POWPLOT**. Give a suitable title such as **'Nickel Powder Data Input'**. The character cases will be retained. There will be opportunities to change it later. The program will then display the main title, copyright information and the first menu.

```
                 |-----------------------------------------|
                 |       Program EXPEDT Version 6.50       |
                 | A menu driven routine to edit .EXP files |
                 | Distributed on TEST Vers. 20-JUN-1994    |
                 |-----------------------------------------|
       |---------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele           |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
       |                                                               |
       | Copyright, 1994, The Regents of the University of California. |
       |---------------------------------------------------------------|

Experiment title:
         Nickel Powder Data Input
EXPEDT data setup option (<?>,D,K,P,R,S,X) >
```

EXPEDT now gives you some options for the kind of calculation you can setup. Type **'CR'** to see these options explained.

```
EXPEDT data setup options:
 <?> - Type this help listing
 D   - Distance/angle calculation set up
 K n - Delete all but the last n history records
 P   - Powder data preparation
 R   - Review data in the experiment file
 S   - Single crystal data preparation
 X   - Exit from EXPEDT
EXPEDT data setup option (<?>,D,K,P,R,S,X) >
```

You are going to be preparing powder diffraction data so type **'P'**. **EXPEDT** will then take you through the sequence of required steps needed to input powder data.

```
You have no phase information
Select editing option for Powder data preparation (<?>,P,T,X) >
```

EXPEDT now tells you that it has no phase data on file and gives you a short menu of choices. Type **'?'** to see the help listing.

```
The available powder data preparation options are:
 <?> - Type this help listing
 P   - Phases - lattice & sp. group
 T   - Change the experiment title
 X   - Return to the main EXPEDT menu
You have no phase information
Select editing option for Powder data preparation (<?>,P,T,X) >
```

The **'T'** option allows you to change the main descriptive title; all main editing menus in **EXPEDT** have this option available. Your only real option here is to enter phase information so type **'P'**.

```
There is no phase information present
Enter identifying name for new phase number 1.
  >
```

You are reminded that there is no phase information and thus are forced to enter some now. Type a suitable name for this phase, i.e. **'Nickel Powder'**. There is space for 66 characters and the case is retained.

```
No space group information found
Enter space group symbol (ex:  P n a 21, P 42/n c m, R -3 c, P 42/m,
R -3 m R for rhombohedral setting) >
```

Now **EXPEDT** finds that there is no space group information for this phase and it requests a space group symbol. It must be a short or full Hermann-Mauguin symbol such as are found in the International Tables for Crystallography; the axial fields are separated by spaces with subscripts for screw axes following the rotation symbol. No spaces are allowed between the axis symbol and an associated mirror or glide symbol. Some examples are given with the input request. Enter **'f m 3 m'** for nickel; the character cases are converted by **EXPEDT** to conform with the standard, i.e. 'F m 3 m'. **EXPEDT** will interpret the symbol and perform the group theory necessary to generate all needed symmetry information for the space group. This includes the symmetry operations, any special site symmetry constraints, space group extinctions and rules for generation of a unique reflection set. Note that the origin in a centrosymmetric space group is always placed on a center of inversion. Some of these results are then displayed.

```
Space group F m 3 m
The lattice is centric  F-centered cubic         Laue symmetry m3m
 Multiplicity of a general site is 192
 The symmetry of the point 0,0,0 contains 1bar

The equivalent positions are:

 ( 1)     X      Y      Z  ( 2)     Z      X      Y  ( 3)     Y      Z      X
 ( 4)     X      Y     -Z  ( 5)    -Z      X      Y  ( 6)     Y     -Z      X
 ( 7)    -Z      X     -Y  ( 8)    -Y     -Z      X  ( 9)     Y     -Z     -X
 (10)    -X      Y     -Z  (11)    -Z     -X      Y  (12)     X     -Y     -Z
 (13)     Y      X      Z  (14)     Z      Y      X  (15)     X      Z      Y
 (16)     Y      X     -Z  (17)    -Z      Y      X  (18)     X     -Z      Y
 (19)    -Z      Y     -X  (20)    -X     -Z      Y  (21)     X     -Z     -Y
 (22)    -Y      X     -Z  (23)    -Z     -Y      X  (24)     Y     -X     -Z

Enter real lattice parameters (Angstroms)
Enter a >
```

EXPEDT now requests the lattice parameters necessary to describe the unit cell dimensions. In the case of nickel, which is cubic, only the "a" lattice parameter is needed. Type **'3.5234'**; all the lattice parameters are displayed next.

```
Lattice parameters are
    a,b,c  =  3.523400  3.523400  3.523400
    angles =    90.000    90.000    90.000
    volume =    43.741
Lattice symmetry is cubic
Space group symmetry is cubic
Enter phase edit command(<?>,$,D,E,F,M,I,L,S,X) >
```

After one phase has been entered you now have the opportunity for further phase editing commands. Enter **'CR'** or **'?'** to see the full help listing.

```
Phase editing commands:
 <?> - Type this help listing
 $   - Enter DCL command
 D n - Delete all data for phase "n"
 E n - Edit phase data for phase "n"
 F n - Enter unit cell contents data for phase "n"
 I   - Insert new phase
 M n - Toggle magnetic flag for phase "n"
 L   - List phase names
 S n - Enter unit cell sigmas
 X   - Exit to EXPEDT main menu
At least one phase must be defined before leaving this menu
Enter phase edit command(<?>,$,D,E,F,M,I,L,S,X) >
```

As the remark at the end indicates, one phase must have been entered before **EXPEDT** will permit you to exit this section. If you had a two phase mixture, the phase information for the second phase would be inserted with an **'I'** command; the same sequence of questions as above will then appear. You have only one phase in this sample and it has been entered so type **'X'**.

```
You have no data
Select editing option for Powder data preparation (<?>,H,P,T,X) >
```

The message now tells you that there is no diffraction data so the next step is to insert some. The menu has a new item so type **'CR'** to see the new help listing.

```
The available powder data preparation options are:
 <?> - Type this help listing
 H   - Select and prepare histograms
 P   - Phases - lattice & sp. group
 T   - Change the experiment title
 X   - Return to the main EXPEDT menu
You have no data
Select editing option for Powder data preparation (<?>,H,P,T,X) >
```

Select **'H'** to start entering some diffraction data.

```
Input of histograms and modification of histogram controls:
There are no current histograms
Histogram data editing menu (<?>,I,J,X) >
```

You are reminded that there is no data but the menu seems to show two possibilities, type **'CR'** to see what they are.

```
Histogram modification options:
 <?> - Type this help listing
 I   - Insert a new histogram
 J   - Insert a dummy histogram
 X   - Return to previous menu
Histogram data editing menu (<?>,I,J,X) >
```

You may enter either a real data set or generate a dummy data set for test purposes. Here you are going to enter real data so type **'I'**.

```
Enter raw histogram input file name (<?>,$,QUIT)
  >
```

EXPEDT now requests the name of the file that contains the powder diffraction scans for the nickel problem. To see the help listing type **'CR'**.

```
This file must be in standard GSAS powder data format
$    - to enter DCL command
/    - for default (if any)
QUIT - to quit program
*** No file name given ***
Enter raw histogram input file name (<?>,$,QUIT)
  >
```

The normal input at this step is a file name, but if you need help in recalling the name of the file you can enter a VMS (or UNIX) command to locate it. In this case the file GSAS_EXERCISES:NICKEL.RAW contains four powder diffraction patterns each obtained from one of the four counter banks of a 10m neutron powder diffractometer at LANSCE. This file is a fixed record length ASCII file constructed so that it can be read by **EXPEDT** and **POWPREF**. The format of this file is described in the **GSAS** technical manual. It is usually generated by site specific programs designed to take data from the instrument and convert it into the proper format adding appropriate information required by **GSAS** programs. Enter **'GSAS_EXERCISES:NICKEL.RAW'** (UNIX name **'/usr/gsas/gsas_exercises/NICKEL.RAW'** - note the cases used in this name).

```
Header on file:
  NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Is this the correct file (<Y>/N/Q)? >
```

EXPEDT prints the data set title and asks if it is the correct one. If you answer **'N'**, it will ask for another data file name; the **'Q'** option is used to exit from **EXPEDT**. This title is taken from one of the records in GSAS_EXERCISES:NICKEL.RAW and originated from a title given when the data was collected. Since this is the correct data set type**'CR'**.

```
Enter POWDER instrument parameter file name (<?>,$,QUIT)
  >
```

You are now requested to enter the name of a file that contains instrument specific information. Type **'CR'** to see the help listing.

```
This file must be in standard GSAS ISAM format
$    - to run DCL command
/    - for default (if any)
QUIT - to exit from program
Enter POWDER instrument parameter file name (<?>,$,QUIT)
  >
```

Again you can enter VMS (or UNIX) commands to help locate the proper file name. The proper filename for this exercise is **'GSAS_EXERCISES:INSTPARM.TOF'** (or **'/usr/gsas/gsas_exercises/INSTPARM.TOF'**). Enter this name.

```
The raw data file is : gsas_exercises:nickel.raw
Enter bank number desired (<0 for list, 0 to quit) >
```

As noted above the data set in NICKEL.RAW contains four powder diffraction patterns, one from each of four 'banks' of detectors. To see the characteristic 2Θ values for each of the banks type **'-1'**.

```
Available banks of data:
Bank  1 DIFC =     789.51 2-theta =     13.880
Bank  2 DIFC =    4368.97 2-theta =     88.050
Bank  3 DIFC =    5829.29 2-theta =    148.290
Bank  4 DIFC =    5821.89 2-theta =    148.290
The raw data file is : gsas_exercises:nickel.raw
Enter bank number desired (<0 for list, 0 to quit) >
```

You will use banks 2 and 3 for this exercise, so type **'2'** to read the data from the 90° bank. There will be a pause while **EXPEDT** reads ~5000 data points for this powder pattern.

```
Reading histogram - please wait
Bank  2 DIFC =    4368.97 2-theta =     88.050
Do you wish to preview this histogram (Y/<N>)? >
```

As a final check on the quality of the data you may preview the raw powder pattern. If you type **'Y'**, the entire pattern will be plotted. After the plot you have another chance to reject the data and choose a different bank number. For now assume the data is OK and type **'CR'**.

```
Editing of histogram information:

Histogram no.   1 Bank no.  2 Two-theta =    88.05
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram is not ready to be used in least-squares
Minimum d-spacing must be set before processing by POWPREF
The data compression factor is  1
The data sampling factor is  0
There are     0 channels in the profile
There are  5120 channels in the spectrum
The first     0 channels are not used
Enter histogram data modification command (<?>,A,B,C,D,E,F,I,L,P,S,T,W) >
```

EXPEDT has now given you the full title and a description of the first data set and a comment concerning its status. Also listed is some information about the size of the data set; the compression factor of one means that every channel in the data set will be used individually. Type **'CR'** or **'?'** to see the full help listing for this menu.

```
Histogram editing commands:
 <?> - Type this help listing
 A - Edit sample orientation angles
 B   - Edit fixed background
 C   - Edit the data compression factor
 D   - Set minimum d-spacing - REQUIRED for new histograms
 E   - Edit excluded regions
 F   - Set phase flags for this histogram
 I   - Edit instrumental constants
 L   - List histogram title
 P   - Plot histogram
 S   - Edit the data sampling factor
 T   - Set min TOF or max 2-Theta (equivalent to D option)
 W   - Edit profile params.
Enter histogram data modification command (<?>,A,B,C,D,E,F,I,L,P,S,T,W) >
```

Notice that this menu has no exit (**'X'**) command; this is because the minimum d-spacing must be set first by either the **'D'** or **'T'** options. However, it is helpful to display the powder pattern when setting the minimum d-spacing. Type **'P'** to display this histogram.

```
Enter terminal type (<?>,A,B,C,D,E,F,G,H,Z) >
```

You must now enter the type of graphics terminal you are now working on; type **'?'** to see the list of supported terminals.

```
Terminal types supported for graphics:
 A  DEC VT100 with RETROGRAPHICS
 B  Tektronix 4105/VersaTerm PRO
 C  Tektronix 4010/4014
 D  DEC VT240/VT330/VT340 Regis graphics (black background)
 E  Pericom emulation
 F  DEC VT240/VT330/VT340 Regis graphics (white background)
 G  X-Windows/Motif workstation (large screen)
 H  X-Windows/Motif workstation (small screen)
 Z  Non graphics terminal
Enter terminal type (<?>,A,B,C,D,E,F,G,H,Z) >
```

If you are not working on a X-Windows workstation then the entries **'G'** and **'H'** will not show in this menu. Choose the appropriate code for your terminal.

```
Do you want to save graphics output (Y,<N>)? >
```

If you respond **'Y'** to this question then the following menu appears. In the present case type **'CR'** and the next two listings will not be seen.

```
Enter hardcopy option (<?>,A,B,C,D,E,F,G,H,J,K) >
```

The various hardcopy devices supported by **EXPEDT** are given in the help listing.

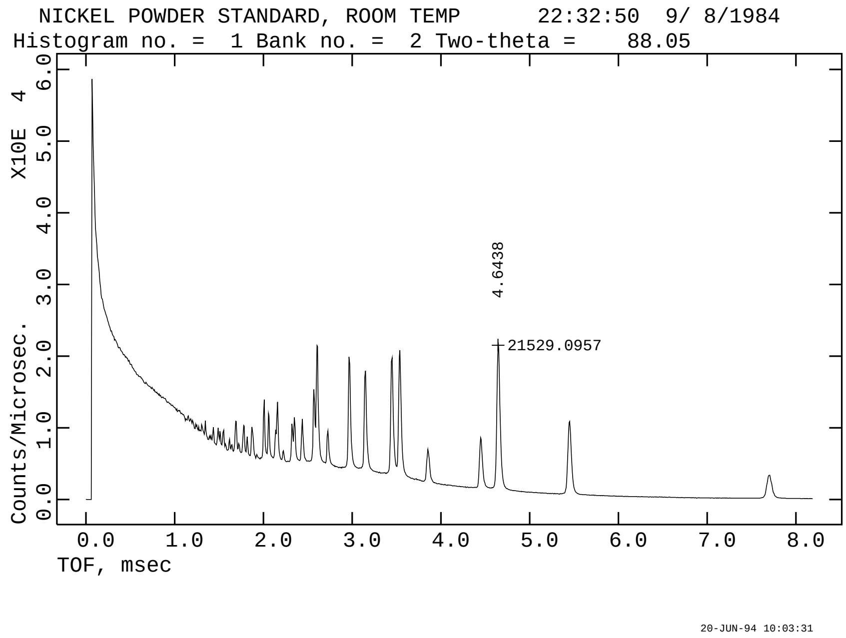
```
High resolution hardcopy device:
 A    LA50 printer
 B    LN03 printer
 C    LN03+ printer
 D    LVP16/HPGL 6-pen plotter 8-1/2x11" paper
 E    LVP16/HPGL 6-pen plotter 11x17" paper
 F    Meta-file output
 G    LN03+ printer, scaled down
 H    PostScript printer
 J    HP Laserjet printer
 K    PostScript file for WORD 5.1a
Enter hardcopy option (<?>,A,B,C,D,E,F,G,H,J,K) >
```

For the selected hardcopy device, the system produces a file named "experiment.device" with the appropriate graphics codes. A new version of this file is opened by each program. To obtain the hardcopy the file must be sent to the appropriate device; this may be attached to the terminal or be a system device. A postprocessor is required to convert "experiment.META" to plots and is not part of **GSAS**. In each case **EXPEDT** will inquire after each plot is displayed whether it is to be added to the file, thus you may select which plots are to be saved.

The next request will appear after your selection of a graphics device.

```
Do you want to set plot ranges for the first plot (Y/<N>)? >
```

After you have gained experience with powder data from a particular diffractometer, then you will have a good idea of what plot range in TOF will allow you to set the minimum d-spacing. You would enter **'Y'** to this question and **EXPEDT** will subsequently ask for a range in TOF (or 2Θ, as appropriate) for the first plot. Since you probably haven't seen this data before, type **'CR'** and the full pattern will be displayed as the first plot.



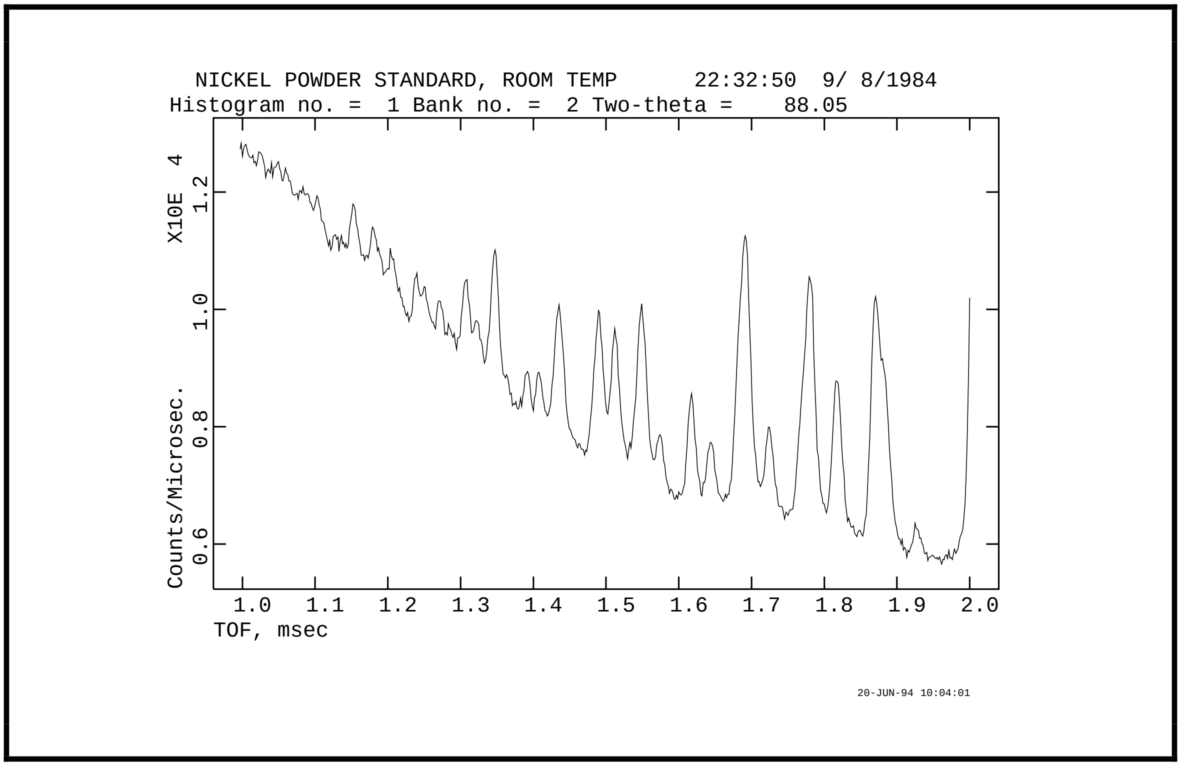
After the plot is finished a graphics cursor will appear. The commands for using this cursor are given at the bottom of the plot; it can be used to find the position and height of a feature in the pattern. For an X-Windows workstation the attached mouse is used to position the cursor and the buttons are active; an additional help message indicates their use. The two figures near the peak at ~4.5 msec were obtained by typing **'W'** and **'H'** after positioning the cursor at the peak top. No return (**'CR'**) is needed for most terminals; you should wait for the cursor to appear before entering a subsequent cursor command. Enter **'X'** (remember no **'CR'**) to exit the cursor mode, a blinking cursor will then appear at the left near the bottom of the screen. If you are working on a VT330 with an attached LA50 printer, you may obtain "screen dump" hard copy on the LA50 by typing **'SHIFT-Print Screen'**. Other terminal/printer combinations will have their own particular scheme for screen dumps. Then type **'CR'** to continue. The following line will appear below the plot:

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

Notice that the plot covers the entire spectrum and includes the very short TOF region. The intensity of the "power pulse" is much higher than the Bragg peaks so you would like to display a more useful region of the pattern. The appropriate response here is to give two values covering some part of the full range of the initial plot. In this case you want to look at the shortest TOF part of powder pattern containing Bragg peaks (1-2 msec) so type **'1 2'**. The following line then appears:

```
Type of scaling desired (<?>,A,R,S) >
```

If you want the new plot to be plotted with the same Y-range as the previous plot then respond **'S'**. If you respond with **'R'**, **EXPEDT** will then request new values for Y-minimum and Y-maximum. You want the plot to be automatically rescaled so type **'A'**. The new plot will then be drawn and should look like:



Again a graphics cursor appears, enter **'X'** (no **'CR'**) to exit the cursor mode and the blinking cursor then indicates that the plot is finished. Type **'CR'** to continue; again you will have the option to view a portion of the initial plot range.

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

Respond this time with **'CR'**. The following menu will appear; the plot is still on the screen.

```
Enter histogram data modification command (<?>,A,B,C,D,E,F,I,L,P,S,T,W) >
```

Now you want to set the minimum d-spacing by setting the minimum TOF. Type **'T'** to select this option; the plot remains on the screen.

```
~  209 reflections for d-minimum & TOF-minimum of  0.250 A &   1.094 msec
Enter new minimum TOF in msec. (/ if OK) >
```

As you can see from the plot, there is very little Bragg intensity above background for TOF < 1.1 msec. Also note that an estimate of the number of reflections from all phases with d-spacings greater than d-minimum is also given. This estimate is always high. Type **'1.1'** for a new minimum TOF. Because the new d-minimum is quite close to the default value, **EXPEDT** will accept the new value and proceed to the next prompt.

```
Histogram no.   1 Bank no.  2 Two-theta =    88.05
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram is not ready to be used in least-squares
Histogram needs to be processed by POWPREF
The data compression factor is  1
The data sampling factor is  0
There are     0 channels in the profile
There are  5120 channels in the spectrum
The first   688 channels are not used
Enter histogram data modification command (<?>,A,B,C,D,E,F,I,L,P,S,T,W,X) >
```

You now see the full title for this histogram and the comment has changed to indicate that the required editing has been performed. This histogram can now be processed by **POWPREF**. Also notice that part of the pattern is now excluded from use; these channels correspond to d-spacings less than d-minimum. The menu now includes the exit option.

Because the diffractometer electronics for this TOF instrument used the same channel width for all banks of detectors, the channel widths for this ~90˚ bank are much narrower than necessary. The compression factor allows you to group adjacent channels together into a single data point for analysis. To change the compression factor type **'C'**.

```
The spectrum has  5120 channels
The current data compression factor is  1
Enter the new data compression factor (1 to 99) >
```

We suggest that you use a compression factor of two so type **'2'**.

```
The new data compression factor is  2
Enter histogram data modification command (<?>,A,B,C,D,E,F,I,L,P,S,T,W,X) >
```

You are finished editing this histogram so type **'X'**; you are still in the process of reading histograms and the next display will show a prompt for a new bank number. The **GSAS** raw data file name is displayed as a reminder.

```
The raw data file is : gsas_exercises:nickel.raw
Enter bank number desired (<0 for list, 0 to quit) >
```

Now you want the data from the third bank of detectors, 2Θ of ~150˚. Type **'3'**, again there will be a pause as ~5000 profile points are read.

```
Reading histogram - please wait
Bank  3 DIFC =    5829.29 2-theta =    148.290
Do you wish to preview this histogram (Y/<N>)? >
```

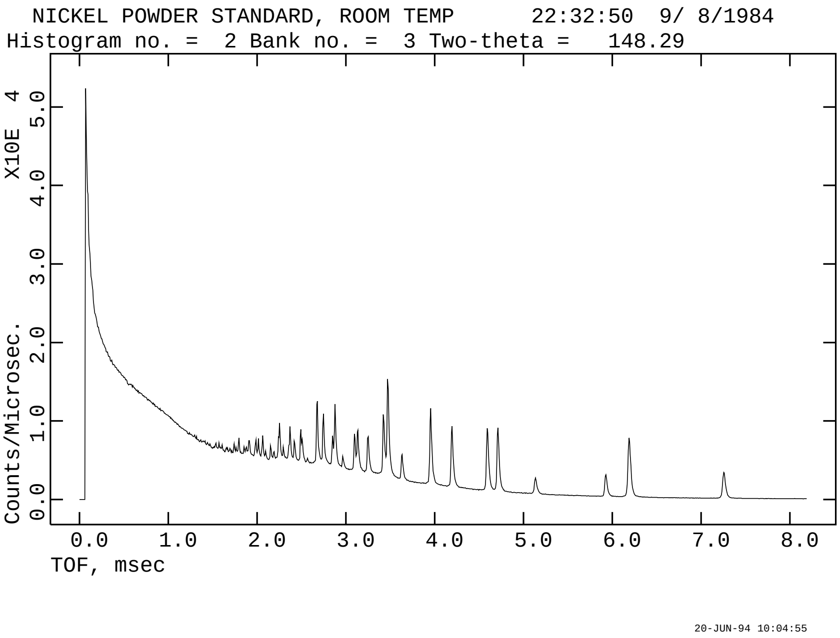
As with the first histogram you can preview the histogram before letting **GSAS** use it; but the data is OK so type **'CR'**.

```
Editing of histogram information:

Histogram no.   2 Bank no.  3 Two-theta =   148.29
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram is not ready to be used in least-squares
Minimum d-spacing must be set before processing by POWPREF
The data compression factor is  1
The data sampling factor is  0
There are     0 channels in the profile
There are  5120 channels in the spectrum
The first     0 channels are not used
Enter histogram data modification command (<?>,A,B,C,D,E,F,I,L,P,S,T,W) >
```

Just as for the first histogram, you cannot exit until the minimum d-spacing has been set. Type **'P'** to plot the pattern.

```
Do you want to set plot ranges for the first plot (Y/<N>)? >
```

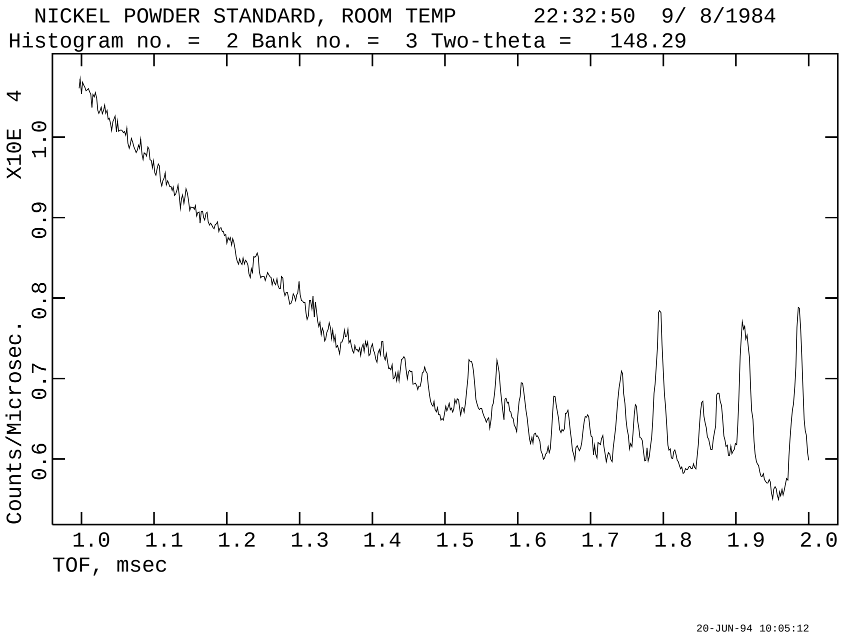
Again you don't know what to expect for this pattern, so type **'CR'**. Since the terminal type is already known to **EXPEDT**, the plot appears immediately.



Again the entire pattern is displayed with the graphics cursor. The "power pulse" is even stronger and you will want to exclude it from the next plot. Type **'X'** and possibly **'CR'** to continue.

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

The useful range starts at 1 msec and you want automatic scaling so type **'1 2 a'**.



Again type **'X'** and possibly **'CR'** to get the next prompt.

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

This plot is satisfactory for setting the minimum d-spacing so type **'CR'** to continue. The menu for editing histogram data will be displayed.

```
Enter histogram data modification command (<?>,A,B,C,D,E,F,I,L,P,S,T,W) >
```

Select **'T'** to set the minimum TOF.

```
~  209 reflections for d-minimum & TOF-minimum of  0.250 A &   1.458 msec
Enter new minimum TOF in msec. (/ if OK) >
```

As you can see from the plot, the first Bragg peaks appear at 1.5 msec so enter **'1.5'** to set the minimum TOF. Because this new minimum is sufficiently different from the default value, **EXPEDT** recalculates the limits and the estimated number of reflections and displays an updated prompt.

```
~  194 reflections for d-minimum & TOF-minimum of  0.257 A &   1.500 msec
Enter new minimum TOF in msec. (/ if OK) >
```

Now type '/' to accept it. The screen will be cleared and the following displayed.

```
Histogram no.   2 Bank no.  3 Two-theta =   148.29
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram is not ready to be used in least-squares
Histogram needs to be processed by POWPREF
The data compression factor is  1
The data sampling factor is  0
There are     0 channels in the profile
There are  5120 channels in the spectrum
The first   937 channels are not used
Enter histogram data modification command (<?>,A,B,C,D,E,F,I,L,P,S,T,W,X) >
```

Again a part of the powder pattern is excluded by the choice of a minimum d-spacing. This powder pattern was collected from a detector bank at a larger 2Θ and has a higher resolution than the first one; thus the compression factor of one is appropriate. Later you may wish to experiment and try various compression factors to see how it affects the calculations. For now leave it at one. The **'W'** option is for access to the Bragg peak shape parameters and related coefficients. The values for these parameters are initially set at appropriate defaults for this instrument and were read from the instrument parameter file. We want you to examine these coefficients and change one of their values so type **'W'**.

```
Change profile parameter values and refinement flags

Histogram no.   2 Bank no.  3 Two-theta =   148.29
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram is not ready to be used in least-squares
Histogram needs to be processed by POWPREF

Phase no. 1
Phase name: Nickel Powder
Aniso. broadening axis   0.   0.   1. Damp  0
Peak profile type no. 1 Number of coefficients: 12
Profile coefficients for Von Dreele, Jorgensen & Windsor convolution function
 J. Appl. Cryst., 15,581-589(1982)
 Modified by Von Dreele - unpublished (1983).
#1(alp-0) =   0.0000 N #3(bet-0) =   5.5766E-02 N #5(sig-0) =    0.00000 N
#2(alp-1) =   0.1374 N #4(bet-1) =   1.3723E-03 N #6(sig-1) =   48.76430 N
#8(rstr ) =     0.00 N #9(rsta ) =         0.00 N #7(sig-2) =    0.00000 N
#10(s0ec) =     0.00 N #11(s1ec) =         0.00 N #12(s2ec) =       0.00 N
Cut-off for peaks is  1.00 percent of the peak maximum
Profile editing options - (<?>,$,A,C,L,P,R,W,X) >
```

There is a set of profile coefficients for each phase and each histogram in a powder data set. The information displayed gives a title identifying the phase and histogram, the identity of the profile function with literature references, the names and values of the coefficients, and a factor setting the limits of the peak bases. It is this last value that we want you to change here. Type **'?'** to see the help listing.

```
Profile editing options:
 <?> - Type this help listing
 $   - Enter DCL command
 A   - Change anisotropic broadening axis
 C   - Change profile parameter values
 L   - List the current profile values and their refinement flags
 P n - Select new phase "n"
 R n - Reset profile coeffs. to default values for type "n"
 W   - Change the peak cut-off value
 X   - Exit from this mode
WARNING--- Changes in profile parameters or cutoff
should be followed by rerunning POWPREF
Profile editing options - (<?>,$,A,C,L,P,R,W,X) >
```

The reason for the warning is that if the profile coefficients are changed significantly or, alternatively, if the cutoff is changed; the range in TOF over which a Bragg reflection contributes may change. **POWPREF** must be rerun in order to establish new peak limits reflecting these changes. You will be running **POWPREF** shortly and the peak limits will be set for the first time. If these parameters or any other parameters that affect reflection positions are changed by the least squares refinement or are manually changed, **POWPREF** should be run again.

The width of the peak base is defined as a cutoff when the peak profile function drops below some fraction of the peak maximum. By default the cutoff occurs when the profile intensity falls below 1.0 percent of the maximum. You are to change that to 0.5 percent so that the peak bases are wider. You can enter the option and the new value on one line so type **'W 0.5'**. **EXPEDT** lists the old and new values.

```
Current cut-off is  1.00 percent of peak maximum
The new cut-off is  0.50 percent of peak maximum
Profile editing options - (<?>,$,A,C,L,P,R,W,X) >
```

You are finished here, type **'X'**.

```
Enter histogram data modification command (<?>,A,B,C,D,E,F,I,L,P,S,T,W,X) >
```

You are all done editing this histogram so type **'X'**. The next display shows that you can read another histogram from the data file.

```
The raw data file is : gsas_exercises:nickel.raw
Enter bank number desired (<0 for list, 0 to quit) >
```

You have read all the data sets that are needed at this time so type **'0'**. If at a later time you want to include more powder patterns, a sequence of menus will bring you back to this section of **EXPEDT**. In addition, if you try to reread a data set for a new histogram **EXPEDT** will warn you of that fact (twice) and give you the opportunity to reconsider.

```
Histogram data editing menu (<?>,D,E,I,J,L,P,R,U,X,Z) >
```

Both histograms are now ready for processing by **POWPREF**. The line displaying the main histogram modification menu now has several additional entries. Type **'?'** to see the full help listing.

```
Histogram modification options:
 <?> - Type this help listing
 D n/n:m - Do not use histograms
 E n - Edit powder histogram "n"
 I   - Insert a new histogram
 J   - Insert a dummy histogram
 L   - List histogram titles
 P n - Edit phase flags for histogram n
 R n - Replace histogram n
 U n/n:m - Use histograms
 Z n - Edit zone data for histogram n
 X   - Return to previous menu
    n/n:m - optional histogram numbers:
    n     - individual histogram number
    n:m   - range of histogram numbers
    ALL   - all histograms
Histogram data editing menu (<?>,D,E,I,J,L,P,R,U,X,Z) >
```

Besides the options for input and modification of histograms, there are two options for flagging specific histograms for inclusion in subsequent calculations. The **'D'** option is used to mark histograms so that they will not be used by **GENLES**, and **'U'** removes that mark. These instructions are only effective on powder data histograms after first processing them with **POWPREF**. You are finished with histogram editing so type **'X'**.

```
Select editing option for Powder data preparation (<?>,H,P,T,X) >
```

You are done with editing of powder data so type **'X'**. The main menu for **EXPEDT** will next appear with some additional entries.

```
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

Once a data set has been introduced to **GSAS** you are able to edit the inputs for least squares and Fourier calculations. Type **'?'** to see these options listed.

```
EXPEDT data setup options:
 <?> - Type this help listing
 D   - Distance/angle calculation set up
 F   - Fourier calculation set up
 K n - Delete all but the last n history records
 L   - Least squares refinement set up
 P   - Powder data preparation
 R   - Review data in the experiment file
 S   - Single crystal data preparation
 X   - Exit from EXPEDT
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

You are all done for now so type **'X'** and **EXPEDT** will terminate and the **GSAS** prompt will be displayed.

```
EXPEDT terminated successfully
  The experiment is NICKEL  creation date = 20-JUN-1994 10:00:04.57
MIST::GSAS Command? >
```

Preparation of Powder Data - Program POWPREF

The next step is to run **POWPREF** to prepare the two histograms just indicated, by generating reflection sets according to the space group and lattice parameters, and matching these sets to the powder patterns. You start with the main **GSAS** prompt.

```
MIST::GSAS Command? >
```

To start it simply type **'POWPREF'** after the **GSAS** prompt. If you are working on a VMS system, you will have the opportunity to choose a batch queue or "online" for running **POWPREF**.

```
Submit POWPREF to which QUEUE? (<ONLINE>,SLOW,SHORT,FAST,OTHER,LIST,?) >?
```

If a previously submitted batch job with this experiment had not finished, an error message will appear telling you that a previous batch file still exists. This message also appears if a previously submitted batch job failed or aborted before completion. In the latter case you must delete the 'EXPERIMENT$PROGRAM.BCH' file before any new batch job can be run. The VMS **GSAS** utility routine **'DBCH'** can be used to delete any batch file for the current experiment. Do not delete the batch file for a batch job that is still running. You now have a choice of batch queues for the **POWPREF** run. Type **'?'** to see the names of the queues.

```
The SLOW queue is SYS$BATCH
The SHORT queue is SYS$MED
The FAST queue is SYS$FAST
OTHER is any legal batch queue name
LIST to list all batch queues
Submit POWPREF to which QUEUE? (<ONLINE>,SLOW,SHORT,FAST,OTHER,LIST,?) >
```

Your VMS system may have a different list, but it will probably have at least a choice between running the job "online", a faster executing queue for short jobs, and a slower one for long ones. The "OTHER" option allows you to enter a specific queue name other than one of the **GSAS** queues. Because this display was produced on a very fast DEC Alpha machine, this menu shows "**ONLINE**" as the default; if selected **POWPREF** would be run immediately giving some brief output showing its progress.

```
POWPREF will be executed online

Histogram no.   1 Bank no.  2 Two-theta =    88.05
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram is not ready to be used in least-squares
Histogram needs to be processed by POWPREF
Header on file:
  NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984

Histogram no.   2 Bank no.  3 Two-theta =   148.29
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram is not ready to be used in least-squares
Histogram needs to be processed by POWPREF
Header on file:
  NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
POWPREF terminated successfully
  The experiment is NICKEL  creation date = 20-JUN-1994 10:00:04.57
MIST::GSAS Command? >
```

For a UNIX system the choice is between running the **POWPREF** job in "foreground" (equivalent to "**ONLINE**") or in the "background". If the job is run in background, a log file with the name 'NICKEL.LOG' is created which will contain the above brief output instead of displaying it on the terminal.

You should wait until **POWPREF** completes before going on to the next step in the training exercise; you should know that any attempt to run certain **GSAS** programs (especially **EXPEDT** and **GENLES**) may destroy sections of the experiment file. **POWPREF** will open a listing file 'NICKEL.LST' which will contain all line printer output from **POWPREF**. Subsequent runs of **POWPREF** and many other **GSAS** programs will append their line printer output onto this file thus generating a continuous record of your progress on the **NICKEL** experiment. If this file is deleted the next one of these programs to be executed will create a new one. The **GSAS** utility **'DLST'** can be used to delete this file. When **POWPREF** completes you can print NICKEL.LST or examine it on your terminal with the **GSAS** utilities **'ELST'** or **'TLST'**. This listing is 132 characters wide so set your terminal accordingly.

Plotting of Powder Data - Program POWPLOT

Introduction

POWPLOT is the routine in **GSAS** for plotting observed and calculated powder diffraction patterns. It also has facilities for displaying the difference curve, performing an error analysis on differences and marking reflection positions. **POWPLOT** can be used to plot any powder pattern once it has been processed by **POWPREF**. This training exercise illustrates its use to check the results of **POWPREF** which you ran in the previous step. You will be interested to see if the calculated reflection positions correspond to the observed peaks; this will be evident from the positions of the reflection markers on the plots.

Running POWPLOT

POWPLOT is run from the **GSAS** command level by entering **'POWPLOT'** after the prompt. The program will display a copyright message and prompt for a letter identifying the kind of terminal you are working on.

```
                  |-----------------------------------------|
                  |      Program POWPLOT Version 6.53       |
                  |     Powder pattern plotting program     |
                  | Distributed on TEST Vers. 20-JUN-1994   |
                  |-----------------------------------------|
       |---------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele           |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
       |                                                               |
       | Copyright, 1994, The Regents of the University of California. |
       |---------------------------------------------------------------|

The last history record is :
    HSTRY  2 POWPREF V-6.17   20-JUN-94 10:07:50
Enter terminal type (<?>,A,B,C,D,E,F,G,H,Z) >
```

Various graphics terminals are supported by **POWPLOT**; they are the same as those in **EXPEDT**. Choose the appropriate code for your terminal.

```
Do you want to save graphics output (Y,<N>)? >
```

If you want to have a hardcopy of the plots (apart from "screen dumps") then respond **'Y'**. We will assume that you entered **'N'**. After listing the experiment title, the main **POWPLOT** menu is shown.

```
Experiment title:
         Nickel Powder Data Input
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

Enter **'?'** or **'CR'** to obtain the full help listing. The screen will be cleared beforehand.

```
POWPLOT Commands:
 <?> - Type this help listing
 B   - Toggle background subtraction control
 C   - Toggle cursor control
 D   - Difference curve toggle
 H n - Read powder histogram "n"
 I   - I/Io or I on Y-axis toggle
 L   - List histogram titles & plot options
 M   - Mark reflection positions toggle
 N   - Read next powder histogram
 O   - Toggle the observed point plotting mode
 P   - Plot histogram
 R   - Plot radial distribution functions
 S   - Set initial plot ranges toggle
 T   - D-spacing or TOF/2-theta on X-axis toggle
 X   - Exit from POWPLOT
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

As you can see many of the options are toggles that switch between two modes; each time one of these is entered the program switches mode and prints a message indicating the current mode. Enter **'L'** to see the list of histogram titles and the current state of all the toggles.

```
The last history record is :
    HSTRY  2 POWPREF V-6.17   20-JUN-94 10:07:50

Histogram no.   1 Bank no.  2 Two-theta =    88.05
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram will be used in least-squares

Histogram no.   2 Bank no.  3 Two-theta =   148.29
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram will be used in least-squares

Background will not be subtracted
Difference curves will not be plotted
Reflection positions will not be marked
Intensities will not be divided by incident spectrum
Plot will use D-spacing in angstroms
Full scale plot will be displayed
Observed points will be plotted as"+"
Cursor will not be active
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

To begin you must read a histogram, enter **'H 1'** or **'N'** to read it. There will be a pause as the file 'NICKEL.P01' is read.

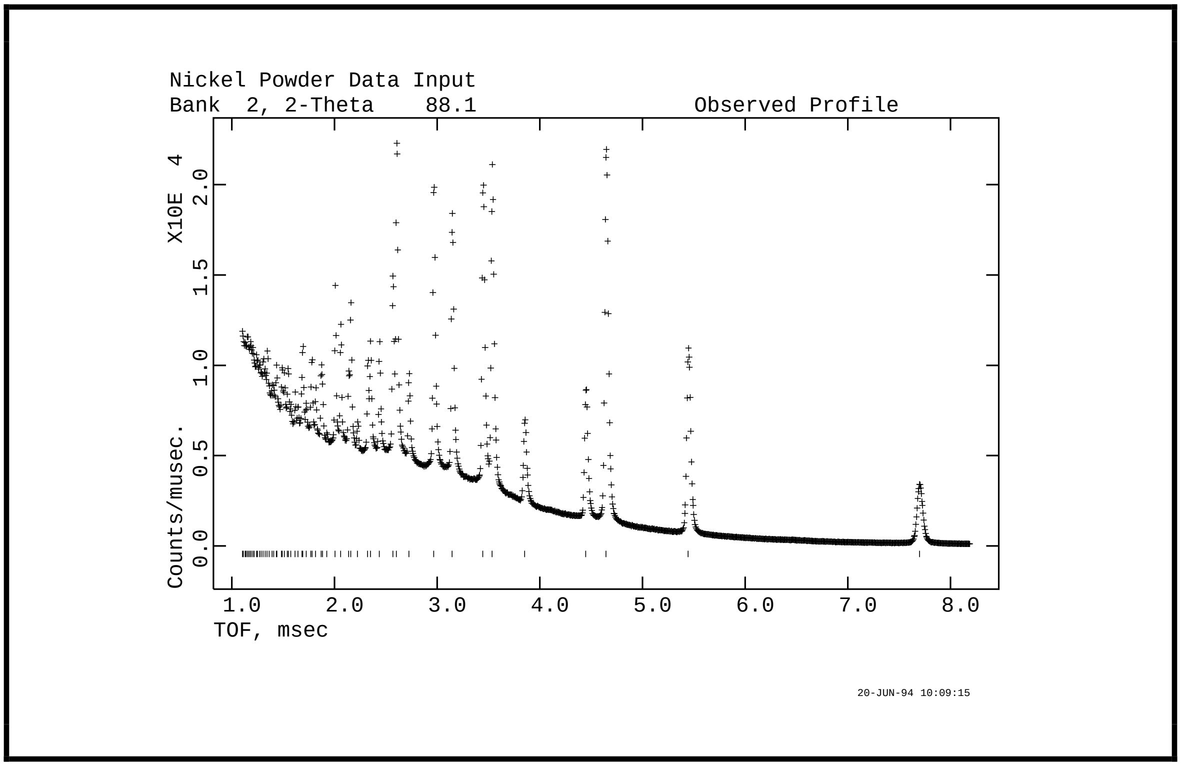
```
The selected histogram is:

Histogram no.   1 Bank no.  2 Two-theta =    88.05
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram will be used in least-squares
Reading histogram - please wait
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

The information displayed gives the histogram number and some information about the histogram to allow you to identify the currently selected pattern. There is also a status message which indicates that this pattern has been fully prepared and is ready to be used for least-squares refinement.

You wish to have the routine mark the reflection positions and use TOF in msec as the X-axis; thus enter **'M T'**. The following messages will be displayed indicating the new state of the appropriate toggle. These toggles will remain set until changed by reentering the appropriate codes.

```
Reflection positions will be marked
Plot will use TOF in msec
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

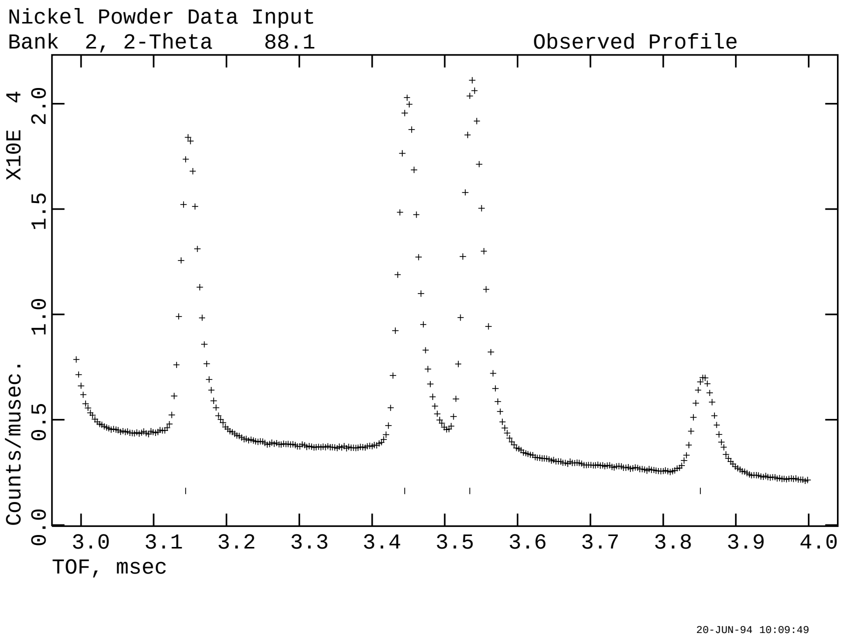
After the toggles have been set as appropriate, enter **'P'** to cause the plot to be drawn on the screen. Assuming that your toggles are set the same way, it should look like this:



After the plot is finished a blinking cursor will appear at the left near the bottom of the screen. Notice that the reflection markers closely correspond to the peak positions. If the lattice parameters or diffractometer zero point had incorrect values the markers would not lie under the peak positions. This situation would probably cause **GENLES** to fail or at best converge very slowly. You would have to correct the values with **EXPEDT** and rerun **POWPREF** before continuing. You may obtain a hard copy if desired with the appropriate command. You may have to type **'CR'** to continue; the following line will appear below the plot:

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

This is generally used for viewing a smaller portion of the plot and operates exactly the same way as the plotting facility in **EXPEDT**. If the **'S'** option had been selected above this line would have appeared before the first plot. You want to look at the region from 3-4 msec with automatic scaling so enter **'3 4 A'**. The new plot will then be drawn and should look like:



Again the blinking cursor indicates that the plot is finished. Notice that the toggle settings are still in force; in order to change these you have to be in the main **POWPLOT** menu. This plot gives you a clearer view of the relationship between the marker positions and the peak tops in this range. It is not essential for the markers to be exactly at the peak top positions for **GENLES** to succeed. In fact, for some of the TOF peak shape functions the proper reflection position is near the left edge of the peak. The kind of agreement that you see here is sufficient. You may have to type **'CR'** to continue; again you will have the option to view a portion of the initial plot range.

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

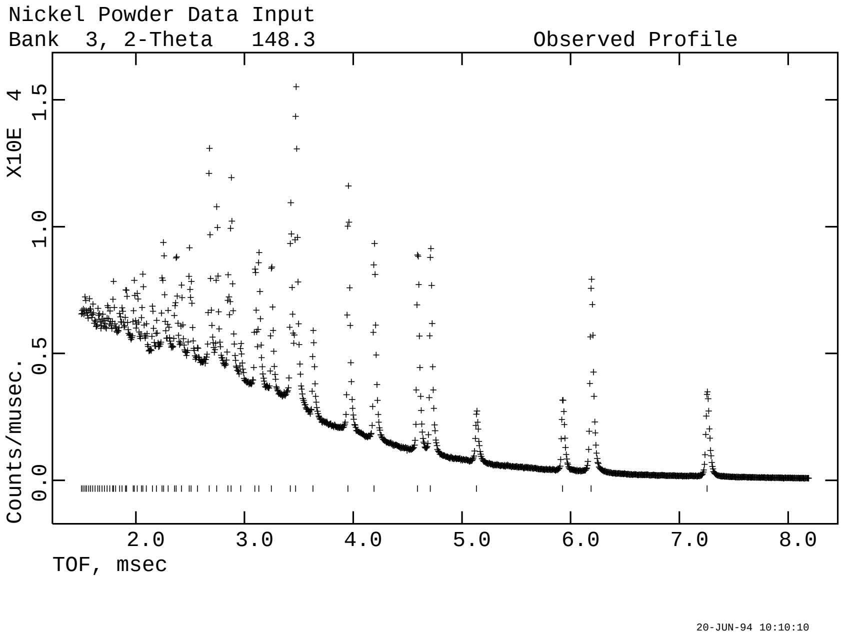
Respond this time with **'CR'**.

```
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

You are now back to the **POWPLOT** main menu and you will want to look at the second histogram. Type **'N'**; the title and status of the second histogram will be displayed. Again there is a pause while 'NICKEL.P02' is read.

```
The selected histogram is:

Histogram no.   2 Bank no.  3 Two-theta =   148.29
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram will be used in least-squares
Reading histogram - please wait
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

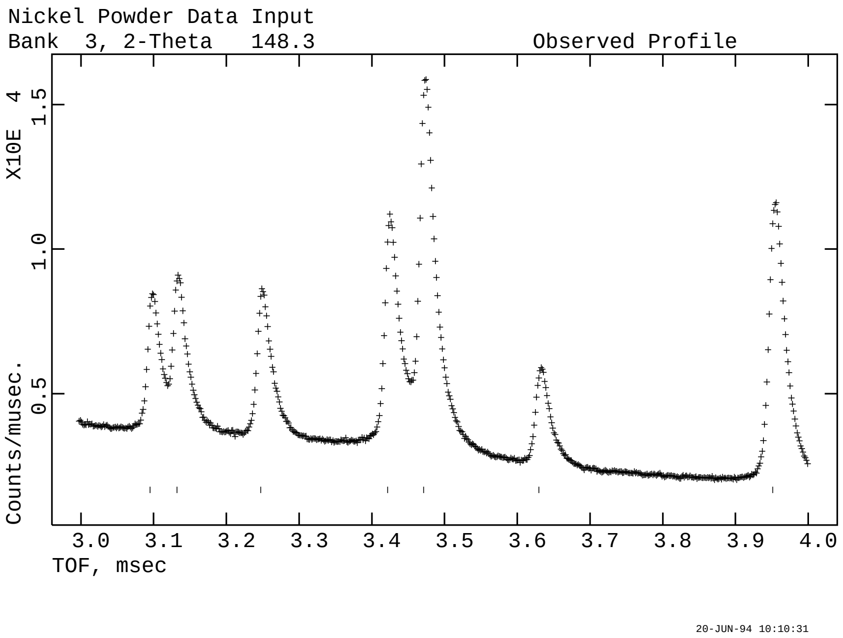
The set of toggles used for the first histogram are still in force; you want to plot this histogram so type **'P'**. The plot will immediately follow.



As before the blinking cursor indicates the plot is finished; type **'CR'** if needed to continue. The following line will appear below the plot:

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

Again you want to look at the powder pattern in the region from 3-4 msec so type **'3 4 A'**. The new plot will then be drawn and should look like:



Again the blinking cursor indicates that the plot is finished. In this plot the marker positions are quite close to the peak center positions and are satisfactory. Type**'CR'** if needed to continue.

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

Respond with **'CR'**.

```
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

You are all done so type **'X'**. **POWPLOT** will terminate and the **GSAS** prompt will appear.

```
POWPLOT terminated successfully
  The experiment is NICKEL  creation date = 20-JUN-1994 10:00:04.57
MIST::GSAS Command? >
```

Setup for Least Squares - Program EXPEDT

Introduction

This training exercise step is needed to enter the data for the first Rietveld refinement cycles for nickel powder. You need to enter the atomic parameters for the nickel atom, set the least squares controls and select a few parameters for refinement. Because all Rietveld refinements start by refining the scale factors and the background coefficients, **EXPEDT** selects these by default along with setting a default number of least squares cycles. Nonetheless, you will examine these parameters to see how they are selected. Once these steps are completed you can run your first least squares.

Running EXPEDT

As before **EXPEDT** is run from the **GSAS** command level by typing **'EXPEDT'**; the experiment name **'NICKEL'** must have previously been selected with the **'EXPNAM'** command. The copyright message will be displayed followed by a summary of your last operation on this experiment and a menu.

```
                  |-----------------------------------------|
                  |       Program EXPEDT Version 6.50       |
                  | A menu driven routine to edit .EXP files |
                  | Distributed on TEST Vers. 20-JUN-1994    |
                  |-----------------------------------------|
        |---------------------------------------------------------------|
        |            Allen C. Larson and Robert B. Von Dreele           |
        |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
        |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
        |                                                               |
        | Copyright, 1994, The Regents of the University of California. |
        |---------------------------------------------------------------|

The last history record is :
    HSTRY  2 POWPREF V-6.17   20-JUN-94 10:07:50
Is this the file you wish to use? (<?>,D,K,N,Q,R,Y) >
```

The 'history record' gives the name and version of the last program in **GSAS** to modify your experiment file. The date and time of that modification is also given. Type **'?'** to see your options.

```
The options here are:
D - Delete this EXP file and look further
K - Live dangerously. NO NEW COPY, NO BACKUP!
N - Look for an older version of the EXP file
Q - Quit, exit from the program
R - Review the data in this file
Y - Create a copy of this file and edit it
Is this the file you wish to use? (<?>,D,K,N,Q,R,Y) >
```

These options allow you to use any of the available versions of the experiment file. For example, if the previous least squares run diverged (as can happen in Rietveld refinements) the **'D'** option allows you to delete the result and go back to a previous version of the experiment file. Thus it is important to be careful about using the VMS command 'PURGE' on these files. The **GSAS** utility **'PEXP'** will purge just the experiment files for the current experiment. If you are very sure of what you are doing and are willing to live with the results of this **EXPEDT** run, you can use the **'K'** option. This saves the step of making a new copy of the experiment file before editing commences. The more cautious response is to create a copy and edit it so type **'Y'**.

```
Experiment title:
         Nickel Powder Data Input
The last history record is :
    HSTRY  2 POWPREF V-6.17   20-JUN-94 10:07:50
EXPEDT data setup option (<?>,D,F,K,L,P,Q,R,S,X) >
```

The experiment title is the one entered in your first session with **EXPEDT**. To see the help listing type **'?'** or just **'CR'**.

```
EXPEDT data setup options:
 <?> - Type this help listing
 D   - Distance/angle calculation set up
 F   - Fourier calculation set up
 K n - Delete all but the last n history records
 L   - Least squares refinement set up
 P   - Powder data preparation
 Q   - Quit EXPEDT; no changes will be made
 R   - Review data in the experiment file
 S   - Single crystal data preparation
 X   - Exit from EXPEDT
EXPEDT data setup option (<?>,D,F,K,L,P,Q,R,S,X) >
```

Because the function of **EXPEDT** is to prepare a data set for a specific type of calculation, the menu lists the different types of calculations possible for a crystal structure analysis. For each selection only that part of **EXPEDT** required to prepare data for that calculation is accessible to you. You want to prepare least squares data so type **'L'**.

```
Select editing option for Least Squares calculation (<?>,A,B,F,L,O,R,S,T,X) >
```

This is the main menu for editing of data for a least squares calculation. Type **'?'** to see the help listing.

```
The available options are:
<?>  - Type this help listing
 A   - Edit atom parameters
 B   - Edit rigid body constraints
 F   - Edit atom form factor parameters
 L   - Edit least squares controls
 O   - Edit overall parameters
 R   - Review some of the EXP file data
 S   - Edit soft constraint data
 T   - Change the experiment title
 X   - Exit to main EXPEDT menu
Select editing option for Least Squares calculation (<?>,A,B,F,L,O,R,S,T,X) >
```

As you can see the options listed here cover those things that are essential for the setup of a least squares run. You can edit atom parameters (you will do that after changing the title), set the least squares controls (number of cycles, etc.), edit overall parameters (scales, lattice parameters, profile coefficients, etc.) and finally examine the records in the experiment file to see what has been done. To change the title type **'T'**.

```
Old experiment title:
Nickel Powder Data Input
Enter new experiment title (/ if OK)
  >
```

So that the next set of titles reflect the status of the nickel problem enter **'Nickel Powder Refinement'**.

```
Select editing option for Least Squares calculation (<?>,A,B,F,L,O,R,S,T,X) >
```

Since you need to enter a nickel atom, type **'A'**.

```
Phase No. 1 There are   0 atoms for this phase
Title: Nickel Powder
Give atom editing command (<?>,$,I,S,X) >
```

The lines just displayed tell you that for the nickel powder phase you do not have any atoms. As you can see there is only one atom editing option; type **'?'** to see the help listing.

```
Atom editing commands:
 <?>               - Type this help package
 x <?>             - To give details on command x
 $                 - Enter DCL command
 I s               - Insert one atom or read atoms from a file
 S                   - Modify the space group and unit cell data
 X                 - Exit from editing atoms
Where "t" is an atom type, "s" is an atom sequence number, "s1:s2" refers
to a range of atom sequence numbers, and "codes" are specific to the
command; see the individual help listings for specific instructions

Phase No. 1 There are   0 atoms for this phase
Title: Nickel Powder
Give atom editing command (<?>,$,I,S,X) >
```

As you can see when there are no atoms your only options are to either insert one or exit. You want to enter the one nickel atom needed for this problem so type **'I 1'**. You are then prompted for some information about atom '1'.

```
Enter TYPE, X, Y, Z, FRAC or <?> for help
  >
```

You are prompted to enter the atom 'TYPE' first. This is just the chemical symbol for the atom; **EXPEDT** uses this symbol to search an atom data file for all information available for that element and place that data in the experiment file for later use. The main computational programs such as the least squares program **GENLES** use the atom TYPE to retrieve scattering factor data or other data as needed. If the TYPE is unknown **EXPEDT** will prompt you for a new one, but you should note that character case for TYPE is not significant. The TYPE can also be used to select isotope and ion specific information; a TYPE of **'NI+2_58'** (note the underscore '_') would load the Ni^{2+} x-ray and the ^{58}Ni neutron scattering data. Specifying a TYPE of just **'NI'** gives the neutral atom x-ray scattering factor and the natural abundance neutron scattering length. Note the ion charge is specified before the isotope and synthetic elements (Pu etc.) have no 'natural abundance' and therefore require the isotope designator.

The next three entries are the crystallographic fractional coordinates for the atom and are usually entered as decimal numbers but in some cases integer fractions are more useful (i.e. 1/3 1/3 1/3 instead of .333333 .333333 .333333). The last entry 'FRAC' is the fractional occupancy of the atom site. Normally a given atom site is occupied by an atom 100% of the time, thus FRAC = 1.0. However, either due to disorder or solid solution formation, a given atom site is sometimes occupied only part of the time by a particular type of atom. FRAC is then set to that fraction. Note that this value does not have to be adjusted by the number of symmetry equivalent sites in the cell. **GSAS** programs automatically handle the site symmetry and multiplicity so you need not be concerned about its effects on FRAC. To enter the appropriate values for the nickel atom type **'NI 0 0 0 1'**.

```
Enter optional name (/ for default = NI(1)   ) >
```

EXPEDT composes an optional name for your reference. It is constructed from the atom element symbol and sequence number. You may replace it with another if you desire. The optional names are 8 characters wide and can not contain imbedded blanks or commas. You assume that this one is OK so type **'/'**.

```
Enter FLAG (I or A) and U's (<?> for help) >
```

The 'FLAG' requested is to tell **EXPEDT** whether you are going to enter an **'I'**sotropic temperature factor, U_{iso}, or a set of six **'A'**nisotropic temperature factors; u_{11}, u_{22}, u_{33}, u_{12}, u_{13} and u_{23}. Anisotropic temperature factors are checked to ensure that they are consistent with the atom site symmetry and are corrected if they do not conform. You are going to enter just a single isotropic value for this nickel atom so type **'I 0.004'**. A listing of the atom data just entered is displayed next.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM  MULT FXU
  1 NI   0.00000 0.00000 0.00000 1.00000 NI(1)    0.00400 I       M3M     4 000

Phase No. 1 There are   1 atoms for this phase
Title: Nickel Powder
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

The atom data is listed in essentially in the same order as it was input. Notice the extra spaces after 'I' in the column marked 'CODE'; these are places for atom refinement codes. Later you can refine atom parameters and the codes 'F', 'X', 'U' will appear here to indicate that these classes of atom parameters are subject to refinement. **GSAS** handles the symmetry rules governing the refinement of atom parameters, therefore only the parameter class to be refined need be noted. The columns marked 'STSYM' and 'MULT' give the site symmetry and the number of equivalent positions in the cell for this atom location. The last column marked 'FXU ' gives the damping factors for each of these classes of atom parameters. This type of listing is also produced after most other atom editing commands. Also notice that the atom editing menu has grown considerably in length; type **'CR'** to see the full help listing.

```
Atom editing commands:
 <?>               - Type this help package
 x <?>             - To give details on command x
 $                 - Enter DCL command
 +,-,*, or /       - Modify num. atom parameters
 C t/s/s1:s2 codes - Change atom parameters
 D t/s/s1:s2 codes - Modify atom damping factors
 E t/s/s1:s2       - Erase atoms
 F                 - Fix specific atom parameters
 I s               - Insert one atom or read atoms from a file
 K                 - Set atom parameter constraints
 L t/s/s1:s2       - List atoms, if none specified all atoms will be listed
 M                 - Edit magnetic moment data
 S                 - Modify the space group and unit cell data
 T t/s/s1:s2 M V   - Transform atom parameters by matrix "M" and vector "V"
 U t/s/s1:s2 codes - Convert atom thermal factors
 V t/s/s1:s2 codes - Modify refinement flags
 X                 - Exit from editing atoms
Where "t" is an atom type, "s" is an atom sequence number, "s1:s2" refers
to a range of atom sequence numbers, and "codes" are specific to the
command; see the individual help listings for specific instructions

Phase No. 1 There are   1 atoms for this phase
Title: Nickel Powder
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

This help listing gives a short description of how each command works. Note that a command letter alone or followed by **'?'** gives a help listing specifically for that command. Try this with each command to see the various help listings. Notice the reference to atom sequence number. As each atom is entered you assigned it a unique sequence number in the range 1-999; **EXPEDT** checks it for uniqueness. It retains this number for all subsequent manipulations; i.e. it cannot be changed (except by **UNIMOL**). After one atom has been inserted subsequent atoms can be added in sequence by entering **'I N'**. When you want to edit some parameters associated with this atom you must refer to it with this number. However, groups of atoms can be referred to by either a range of sequence numbers (i.e. **4:20** for atoms 4 to 20, inclusive) or by atom type (i.e. **C** for all carbon atoms). As a consequence some of the atom editing commands are quite powerful (and dangerous - particularly **'C'**). You have successfully entered the required nickel atom so type **'X'** to return to the main least squares editing menu.

```
Select editing option for Least Squares calculation (<?>,A,B,F,L,O,R,S,T,X) >
```

Next you want to examine the least squares controls so type **'L'**.

```
Maximum number of cycles is   3
Enter L-S control editing option (<?>,C,E,L,P,X) >
```

The only required least squares control for a Rietveld refinement has already been set, namely the number of least squares cycles to be performed. Type **'?'** to see the help listing.

```
 C n - maximum number of cycles
 E   - Change powder data Fobs extraction flags
 L   - List current settings
 P   - Select options for the output listing
 X   - Exit from editing least squares controls
Enter L-S control editing option (<?>,C,E,L,P,X) >
```

The **'E'** option allows you to extract "observed" structure factors from the Rietveld refinement in **GENLES**. They are calculated by apportioning the observed profile intensity among the contributing reflections according to the ratio of the calculated structure factors. These calculated values are either obtained using the atom parameters or derived by the leBail procedure, where the calculated structure factors are obtained from the set of observed values extracted in the previous refinement cycle. The **'P'** option allows you to request additional information beyond the default to be printed in the **GENLES** list output. You are done here so type **'X'** to go back to the main menu.

```
Select editing option for Least Squares calculation (<?>,A,B,F,L,O,R,S,T,X) >
```

Next you want to check the overall parameters so type **'O'**.

```
Enter overall parameter to be edited (<?>,A,B,C,E,H,L,O,P,S,X) >
```

For the case of powder data there are several classes of overall parameters and the options listed in this menu cover each of these. Type **'?'** to see the help listing.

```
Overall parameters editing options:
 <?>  - Type this help listing
 A   - Absorption coefficients
 B   - Background coefficients
 C   - Diffractometer constants
 E   - Extinction parameters
 H   - Histogram scale factors
 L   - Lattice parameters
 O   - Preferred orientation parameters
 P   - Profile coefficients
 S   - Phase and element fractions
 X   - Exit from editing overall parameters
Enter overall parameter to be edited (<?>,A,B,C,E,H,L,O,P,S,X) >
```

As you can see each kind of overall parameter has its own editing option. Because this is the first editing session for least squares preparation, **EXPEDT** has set reasonable defaults for each of the overall parameters. You have already seen the set of profile coefficients for the second histogram; these were taken from the instrument parameter file 'INSTPARM.TOF'. Other values are set to 1.0 or 0.0 as appropriate. Each overall parameter has its own refinement flag; these are set from within each editing option. **EXPEDT** has by default set the flags for the scale factors, one for each histogram, and the background coefficients, four per histogram. You are now going to look at the background and scales editing options to see how they work. Type **'B'** to invoke the background editing option.

```
Editing of background parameters

Histogram no.   1 Bank no.  2 Two-theta =    88.05
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram will be used in least-squares
Power series in Q**2n/n! function (#4)
Background parameters:
 Refinement flag = Y  Damping flag = 0  Full background (Y)

   0.100000E+01   0.000000E+00   0.000000E+00   0.000000E+00
Give background parameter edit command (<?>,B,C,D,F,G,H,K,L,N,V,X) >
```

EXPEDT displays the background information for the first histogram along with its title and characteristic data. Notice that the 'Refinement flag' equals 'Y'; this means that these background coefficients will be refined by the least squares program. Also notice that four values are shown, 1.00000 and three zeros. These are the default values chosen by **EXPEDT**; they can be changed if desired. The **GSAS** system permits use of up to 36 background coefficients but it is best to start with four and see if more are needed later. Type **'?'** to see the help listing.

```
Background edit commands:
 <?> - Type this help listing
 B   - Modify the full background refinement flag
 C   - Allows changes to the number of background terms and their values
 D n - Enter refinement damping factor "n" (n = 0 to 9)
    The applied shift is (10-n)*10% of the computed shift, n = 0 for full shift
 F   - Fix specific background parameters
 G   - Global setting of refinement flags
 H m - Select histogram "m"
 K b - Set constraints for background coeff. "b"
 L   - Lists the background parameters and refinement flag
 N   - Select next powder histogram
 V   - Toggle background refinement flag
 X   - Exit to overall parameter menu
Give background parameter edit command (<?>,B,C,D,F,G,H,K,L,N,V,X) >
```

As you can see each of these options covers a specific kind of operation to be performed on the background parameters. Notice that there are two options for switching histograms, **'H'** and **'N'**. The latter one is most convenient because it simply steps to the next histogram. Since everything is correct for the first histogram, type **'N'** to move to histogram 2.

```
Histogram no.   2 Bank no.  3 Two-theta =   148.29
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram will be used in least-squares
Power series in Q**2n/n! function (#4)
Background parameters:
 Refinement flag = Y  Damping flag = 0  Full background (Y)

   0.100000E+01   0.000000E+00   0.000000E+00   0.000000E+00
Give background parameter edit command (<?>,B,C,D,F,G,H,K,L,N,V,X) >
```

The same kind of information is displayed for the second histogram; again the refinement flag is set and there are four coefficients for the background function. This is also satisfactory; type **'X'** to return to the overall parameter editing menu.

```
Enter overall parameter to be edited (<?>,A,B,C,E,H,L,O,P,S,X) >
```

You now want to examine the scale factors for the two histograms so type **'H'**.

```
Editing histogram scale factors

Histogram no.   1 Bank no.  2 Two-theta =    88.05
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram will be used in least-squares

Histo. scale =      1.0000     Refine Y Damping flag =  0
Histogram scale editing options - (<?>,C,D,G,H,K,L,N,V,X) >
```

In very much the same form that was used for the background parameters, **EXPEDT** displays the scale factor for the first histogram. By default the scale is set to 1.000 and the refinement flag is set. Type **'?'** to see the help listing.

```
Histogram scale editing options
 <?> - Type this help listing
 C   - Change histogram scale
 D   - Change the histo. scale damping factor
 G   - Global setting of refinement flags
 H m - Select new histogram "m"
 K   - Set histo. scale constraints
 L   - List the current histo. scale and refinement flag
 N   - Select next histogram
 V   - Toggle refinement flag
 X   - Exit to overall parameter editing menu
Histogram scale editing options - (<?>,C,D,G,H,K,L,N,V,X) >
```

The options are similar to those for background. Since the scale factor data for the first histogram is correct, step to the second by typing **'N'**.

```
Histogram no.   2 Bank no.  3 Two-theta =   148.29
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram will be used in least-squares

Histo. scale =      1.0000     Refine Y Damping flag =  0
Histogram scale editing options - (<?>,C,D,G,H,K,L,N,V,X) >
```

As for the first histogram, the default scale is 1.000 and the refinement flag is set. This is also correct so type **'X'** to return back to the overall parameter menu.

```
Enter overall parameter to be edited (<?>,A,B,C,E,H,L,O,P,S,X) >
```

There are no other overall parameters that need to be examined at this time so type **'X'** to return to the main least squares menu.

```
Select editing option for Least Squares calculation (<?>,A,B,F,L,O,R,S,T,X) >
```

You have successfully completed the editing for this first least squares refinement so type **'X'** to return to the main **EXPEDT** menu.

```
EXPEDT data setup option (<?>,D,F,K,L,P,Q,R,S,X) >
```

There is no other data to be setup so type **'X'** to exit **EXPEDT**; the **GSAS** prompt will then appear.

```
EXPEDT terminated successfully
  The experiment is NICKEL  creation date = 20-JUN-1994 10:14:52.14
MIST::GSAS Command? >
```

Refinement of Powder Data - Program GENLES

The next step is to run **GENLES** and refine the selected parameters for the 'NICKEL' problem, namely the two scale factors and eight background parameters. **GENLES** is usually run as a batch job; to start it simply type **'GENLES'** after the **GSAS** prompt. In VMS **GSAS** will then inquire which queue you want to run it in.

```
Submit GENLES to which QUEUE? (<ONLINE>,SLOW,SHORT,FAST,OTHER,LIST,?) >
```

Although the "online" option is also available for **GENLES**, we will assume that you have chosen a batch queue. **GSAS** will then inquire whether you want a log file.

```
Do you want the log file for GENLES? (Y,<N>,K,?) >
```

All batch jobs in **GSAS** can produce a log file with the name 'EXPERIMENT$PROGRAM.LOG'. This file is retained in the directory containing the experiment file; i.e. it is not printed by the system. It is also possible to list it using the utility routine **'TLOG'** while the job is running so that the progress of the job can be monitored. Some **GSAS** batch programs write significant information, warning and error messages into the log file and can thus be examined before the job is completed. To see the help listing type **'?'**

```
LOG file menu:
  Y  = Create a log file, purging all old LOG files for this experiment
  N  = No LOG file, no purge of old LOG files
  K  = Create a new LOG file and KEEP all existing LOG files

Do you want the log file for GENLES? (Y,<N>,K,?) >
```

The options here will determine what will happen to the log file for this run and all previous log files for this experiment. Enter an appropriate option.

```
Job NICKEL_GENLES (queue SYS$MED, entry 266) started on SYS$MED
  The experiment is NICKEL  creation date = 20-JUN-1994 10:14:52.14
Job NICKEL_GENLES (queue SYS$MED, entry 266) completed
MIST::GSAS Command? >
```

A batch job will be submitted with the name 'NICKEL_GENLES'.

For a UNIX version of **GSAS** the choice will be between running **GENLES** in foreground or background. As was the case for **POWPREF** above, **GENLES** will give brief messages showing its progress. These will appear on the terminal for foreground running or on the log file 'NICKEL.LOG' for background running.

The running time for this job will be a few seconds to 5 minutes depending on your system; turnaround time will be a little longer. As with **POWPREF**, wait for **GENLES** to finish before continuing on with the training exercise. **GENLES** will append its output to the listing file 'NICKEL.LST' which also contains all line printer output from **POWPREF**. When **GENLES** completes you can print NICKEL.LST or examine it on your terminal with the **GSAS** utilities **ELST** or **TLST**. This listing is 132 characters wide so set your terminal accordingly.

Plotting of Results - Program POWPLOT

Introduction

You now will want to examine the results of your first least squares refinement by plotting the observed and calculated powder pattern intensities for the two histograms and examine the differences. This is done with program **POWPLOT**.

Running POWPLOT

Run **POWPLOT** from the **GSAS** command level by typing **'POWPLOT'**. The program will display a copyright message and prompt for a letter identifying the kind of terminal you are working on.

```
                  |------------------------------------------|
                  |      Program POWPLOT Version 6.53        |
                  |     Powder pattern plotting program      |
                  | Distributed on TEST Vers. 20-JUN-1994    |
                  |------------------------------------------|
       |---------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele           |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
       |                                                               |
       | Copyright, 1994, The Regents of the University of California. |
       |---------------------------------------------------------------|

The last history record is :
    HSTRY  4 GENLES  V-6.48   20-JUN-94 10:18:33 Sdsq= 0.688E+05 S/E= 0.804E-05
Enter terminal type (<?>,A,B,C,D,E,F,G,H,Z) >
```

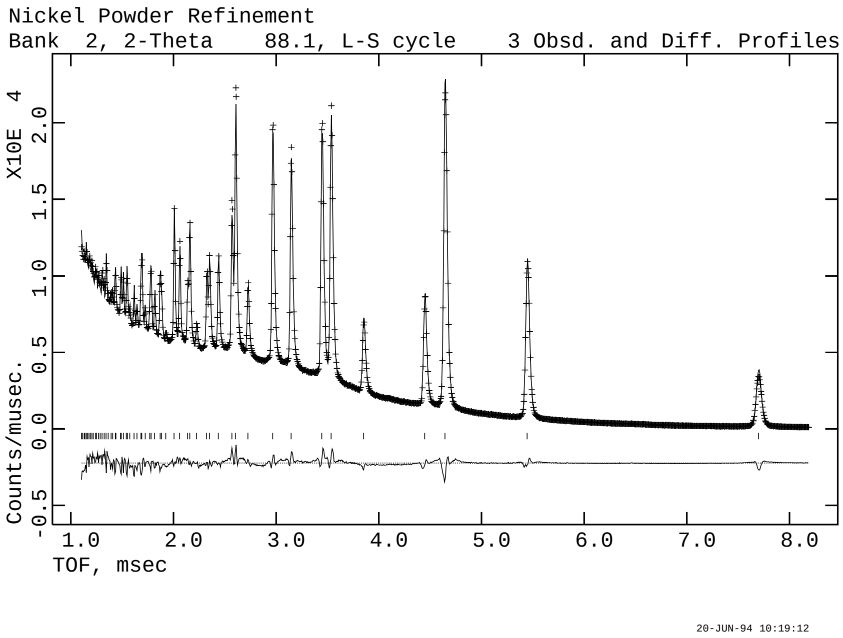
Enter the letter that describes your terminal and respond **'N'** to the hardcopy question. The main menu will be displayed.

```
Experiment title:
         Nickel Powder Refinement
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

Select the first histogram by entering **'N'** or **'H 1'**.

```
The selected histogram is:

Histogram no.   1 Bank no.  2 Two-theta =    88.05
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram will be used in least-squares
Reading histogram - please wait
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

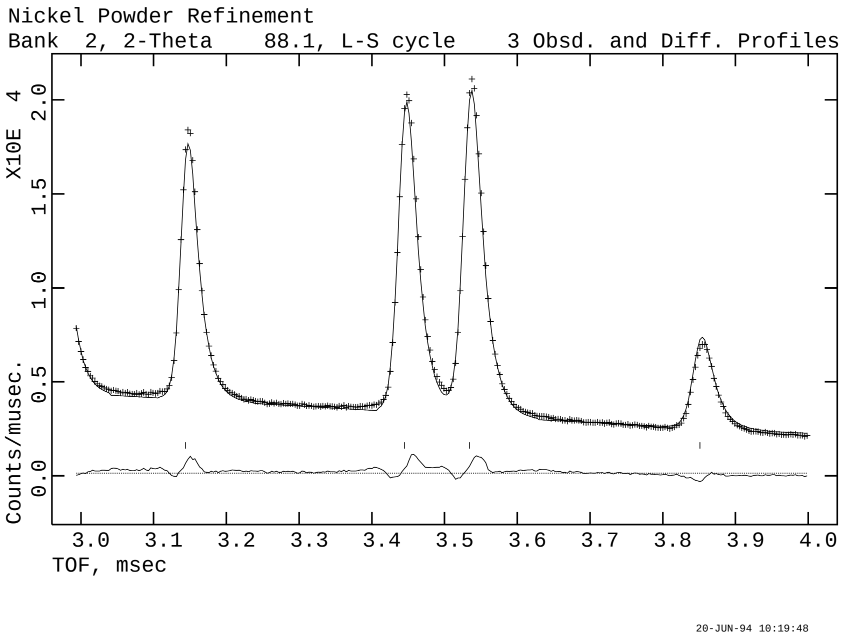
You want to plot the first histogram, display the reflection markers and show the difference curve. You also want the X-axis to show TOF. All of the relevant commands can be entered on one line so type **'M D T P'**. Spaces or commas must separate each entry. Immediately before the plot appears, a few lines will appear as the various toggles are set.



The observed powder pattern intensities are displayed as crosses with the calculated values drawn as a curve. The reflection positions are marked; these are the same as determined by **POWPREF**. The difference curve (I_o-I_c) is displayed near the bottom of the graph with a zero line. The same scale is used for all three sets of plotted values. Clearly there is some remaining residual differences between the two curves, the most obvious is a mismatch in the background at short TOF, and probably additional terms are needed for the background function. To see what other characteristics there are in the differences, you will want to look at a small region of the plot. Type **'CR'** if needed to continue; the following line will appear below the plot:

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

To look at the region from 3-4 msec with autoscaling type **'3 4 A'**. The new plot will be drawn and should look like:



As you can see there is a fairly good match between I_O and I_C. The only difference here is a slight intensity mismatch for each reflection. Type **'CR'** if needed to continue; again you will have the option to view a portion of the initial plot range.

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

Respond this time with **'CR'**.

```
Do you wish to see error analysis (Y/<N>)? >
```

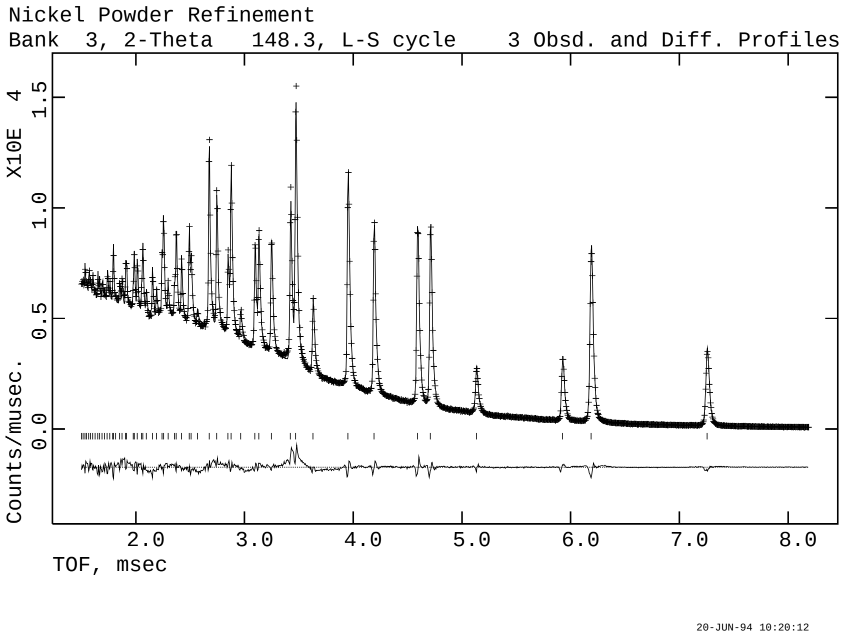
If there is a set of calculated values for the histogram, you have the option of viewing a series of graphs that depict the distribution of differences (I_O-I_C) with, in this case, TOF and compare them with a normal distribution. This is normally only useful when the fit is very close so respond **'N'** this time; we will cover this option for the second histogram.

```
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

You are now back to the **POWPLOT** main menu and you want to look at the second histogram. Type **'H 2'** or **'N'**; the title and status of the second histogram will be displayed.

```
The selected histogram is:

Histogram no.   2 Bank no.  3 Two-theta =   148.29
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram will be used in least-squares
Reading histogram - please wait
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

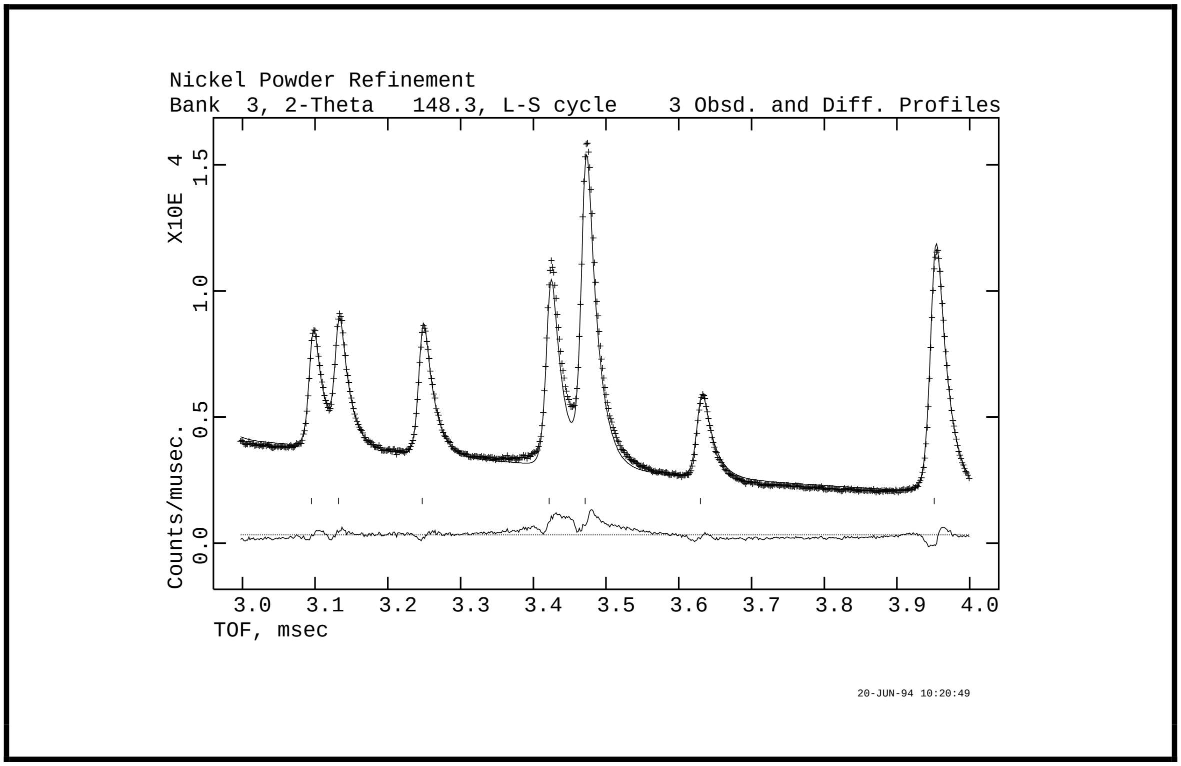
The same set of toggles used for the first histogram are still in force; to plot this histogram type '**P**'. The plot will immediately follow.



In this case the overall fit is much better and the difference curve is much flatter. As before the blinking cursor indicates the plot is finished; type '**CR**' if needed to continue. The following line will appear below the plot:

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

To look at the powder pattern in the region from 3-4 msec with auto scaling type '**3 4 A**'. The new plot will then be drawn and should look like:



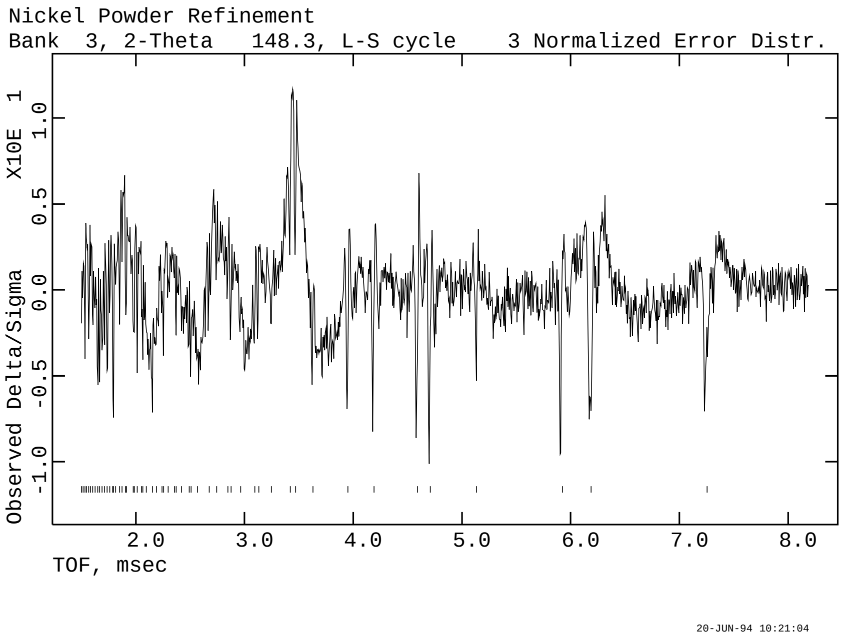
Again the blinking cursor indicates that the plot is finished. The major feature in this difference curve is a broad peak at ~3.45 msec; this is the (111) reflection offset by one TOF frame. Type **'CR'** if needed to continue.

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

Respond with **'CR'**.

```
Do you wish to see error analysis (Y/<N>)? >
```

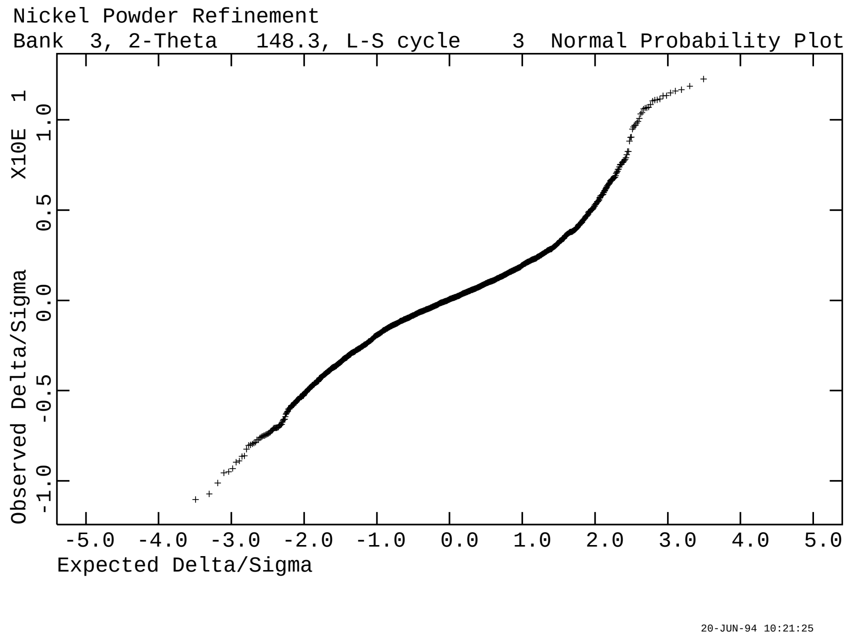
In this case the fit is very good and it is worthwhile doing the error analysis. Type **'Y',** the plot of $(I_o-I_c)/\sigma(I_o)$ verses TOF will immediately follow.



Shown here are the values of (I_o-I_c) divided by $\sigma(I_o)$ plotted against TOF. The most striking feature again is the broad peak at ~3.5 msec; this is the (111) reflection from nickel offset by one TOF frame. Close examination of various regions of this plot can reveal the nature of any other systematics in the differences scaled by esd's. Also notice that the reflection positions are marked; this is because the reflection marker toggle was set for the previous plot. The blinking cursor indicates that the plot is finished. Type **'CR'** if needed to continue.

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

You have the opportunity to examine various regions of this plot; to continue the training exercise type **'CR'**. The next plot is the 'normal probability plot' for this histogram.



As you can see this plot gives a nearly straight line, excepting the extreme positive end, indicating that the I_o-I_c values are for the most part normally distributed. The strong deviation at the high end is from the (111) reflection problem (see Section 4.3 of International Tables for Crystallography, Vol IV for a more complete discussion of normal probability plots). Type **'CR'** if needed to continue.

```
Give X-min and X-max for next plot
 (default plot="0 0" & <CR> for no plot) >
```

You may wish to examine parts of this plot but it is rarely necessary; type **'CR'** to continue.

```
Range of expected deltas to be used for slope/intercept calculation: -2.00  2.00
New values ?(/ to accept) >
```

The program will next compute the slope and intercept for the distribution. The range from -2.0 to 2.0 in expected Δ/σ generally covers the most linear part of the distribution and gives the most useful values; type '/'.

```
The slope & intercept of the normal probability plot are    2.1125    0.0142
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

The high value for the slope is characteristic of an incomplete refinement; as more parameters are refined and a better fit is obtained this value will approach 1.0. The nearly zero intercept indicates that the normal distribution is properly centered about zero. The main **POWPLOT** prompt appears immediately even though the plot remains on the screen. You are all done so type **'X'**. **POWPLOT** will terminate and the **GSAS** prompt will appear.

Suggestions for Further Work on 'NICKEL'

From your examination of the fits for the two powder patterns and the error analyses, you can see that further refinement of the nickel data can improve the results. We suggest that you add more parameters to the least squares refinement as well as try some of the other options in **GSAS**. The first step in continuing the refinement is to use **EXPEDT** to make the appropriate changes to the experiment file. Enter **'EXPEDT'** at the **GSAS** prompt. After the copyright message there will be a history record displayed.

```
                 |------------------------------------------|
                 |       Program EXPEDT Version 6.50        |
                 | A menu driven routine to edit .EXP files |
                 | Distributed on TEST Vers. 20-JUN-1994    |
                 |------------------------------------------|
       |---------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele           |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
       |                                                               |
       | Copyright, 1994, The Regents of the University of California. |
       |---------------------------------------------------------------|

The last history record is :
    HSTRY  4 GENLES  V-6.48   20-JUN-94 10:18:33 Sdsq= 0.688E+05 S/E= 0.804E-05
Is this the file you wish to use? (<?>,D,K,N,Q,R,Y) >
```

GENLES creates a new version of the experiment file which contains the new least squares results. The history record gives a brief summary of the results of the last cycle of least squares along with the date and time that it finished. Because the last least squares gave satisfactory results type **'Y'**; the latest version will be updated. **EXPEDT** copies the experiment file and then gives the title and asks what kind of data preparation you desire.

```
Experiment title:
         Nickel Powder Refinement
The last history record is :
    HSTRY  4 GENLES  V-6.48   20-JUN-94 10:18:33 Sdsq= 0.688E+05 S/E= 0.804E-05
EXPEDT data setup option (<?>,D,F,K,L,P,Q,R,S,X) >
```

Since you are continuing on with more least squares refinement, type **'L'** to continue. Now that you have some familiarity with the operation of **EXPEDT**, you should be able to find your way around the menus quite easily. Use the **'?'** response to see the help listing if you get lost. As a last resort the exit from any menu is **'X'**. If you make a mess of your experiment file, the **'Q'** option in this menu allows you to delete it and, in effect, quit without making any changes.

To further refine the nickel data and improve the fit, you should try adding the following types of parameters to the least squares in the following order.

Background Coefficients

As noted above the first histogram had a poor fit to the background at low TOF's. Thus more background coefficients than 4 are required for a satisfactory fit. We suggest that you add 1 or 2 more for this histogram. The second histogram seems satisfactory but as the fit from adding other parameters improves it may be necessary to add more coefficients here also. You have already been to the background editing menu; it's in the overall parameters menu.

Zero

There is a zero point correction for each histogram, the editing of these is reached by responding **'C'** in the overall parameters menu.

Atom Parameters

For nickel only the isotropic temperature factor can be refined; the setting of the atom refinement flags is reached from the atom editing menu.

Profile Coefficients

The setting of profile coefficient refinement flags is done from the profile editing menu which is reached from the overall parameters menu. You may want to try refining just the 'sig' parameters first; they are profile coefficients 5-7. Don't forget that there is a set for each histogram.

Other Parameters

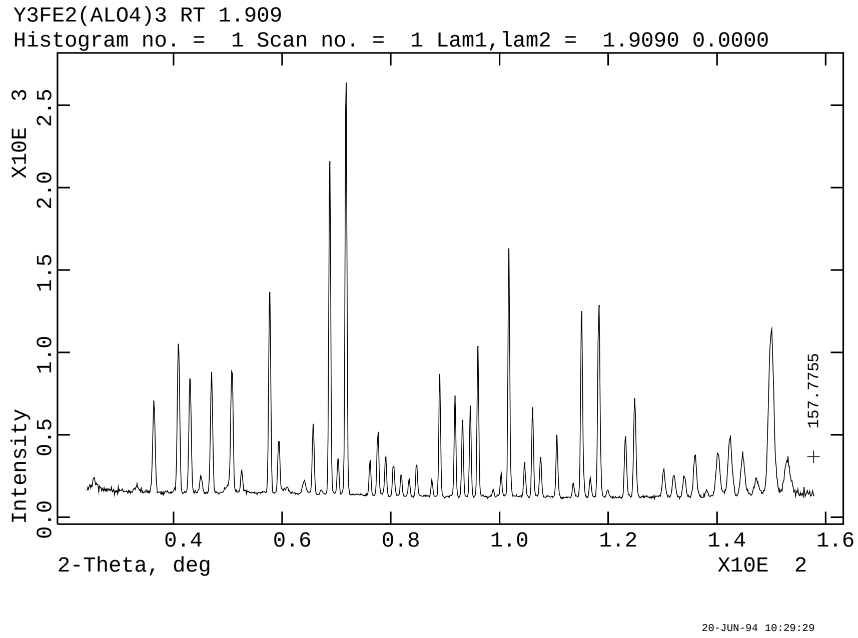
The other parameters that may be refined for the nickel example include the absorption and extinction factors and the lattice parameters. We encourage you to try all of these parameters to get a feel for the sensitivity of the refinement to each of them as well as see how they are edited with **EXPEDT**.

Refinement of Yttrium Iron Garnet

In this training exercise you will refine the structure of a yttrium iron garnet using constant wavelength neutron data . The structure is cubic with four different atomic sites two of which are occupied by both iron and aluminum. The data was taken on the D1a powder diffractometer at the ILL, Grenoble, France using 1.909Å wavelength neutrons. It is presumed that you have already done the nickel powder example and are familiar with many of the facilities in **GSAS**; hence this exercise will only briefly cover those parts. In other parts of this exercise you will be introduced to new features of **GSAS**; and the manual will be more explicit at those points.

Powder Data Setup and Atom Data Entry

The procedure for preparing constant wavelength powder data is essentially identical to that for TOF data as given in the nickel exercise. After entering the **GSAS** command and naming the experiment (**'GARNET'** would be a suitable name) type **'EXPEDT'** to start data preparation. Again the powder data preparation option **'P'** is used to introduce new data to the system. The space group for this garnet is **'I a 3 d'** and the cubic lattice parameter is ca. **'12.19'**. The unit cell contains 24 Y atoms, 16.33 Fe atoms, 23.67 Al atoms and 96 O atoms. This information can be entered into **GSAS** through the phase editing menu. Enter **'F C'** for inserting the chemical formula from the phase editing menu. The raw data can be found in the file **'GSAS_EXERCISES:GARNET.RAW'** (or **'/usr/gsas/gsas_exercises:GARNET.RAW'** for UNIX) and the instrument file is **'GSAS_EXERCISES:INSTPARM.D1A'** (or **'/usr/gsas/gsas_exercises/INSTPARM.D1A'** for UNIX). There is only one histogram corresponding to a scan from 20˚ to nearly 160˚ 2Θ. The scan number for this histogram is **'1'** and the corresponding instrument parameter set is also **'1'**. A plot of the entire histogram is shown below.



The minimum d-spacing sets the upper 2Θ limit for the calculations and is required before you can exit the histogram editing menu. The 2Θ value for end of the scan is noted in the above figure. It is probably easier to set it with the **'T'** option and give a maximum 2Θ of **'159'** which is just beyond the end of the data.

As this was the only histogram to be read you should exit each menu until you reach the **EXPEDT** data setup menu.

```
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

At this point you can continue your editing session by entering **'L'** to start editing of least squares data. As before you will need to enter some atoms, check the least squares controls and perhaps examine the defaults for the other parameters. The atoms you will need to enter are:

```
SER TYPE    X        Y        Z       FRAC   NAME     UISO    CODE  STSYM  MULT FXU
  1 Y    0.12500 0.00000 0.25000 1.00000 Y(1)     0.01000 I    222(100)  24 000
  2 FE   0.00000 0.00000 0.00000 0.60000 FE(2)    0.01000 I     -3(111)  16 000
  3 AL   0.00000 0.00000 0.00000 0.40000 AL(3)    0.01000 I     -3(111)  16 000
  4 AL   0.37500 0.00000 0.25000 0.75000 AL(4)    0.01000 I     -4(100)  24 000
  5 FE   0.37500 0.00000 0.25000 0.25000 FE(5)    0.01000 I     -4(100)  24 000
  6 O   -0.03000 0.05000 0.15000 1.00000 O(6)     0.01000 I        1     96 000
```

This listing is obtained by entering **'L'** after you have entered all the atoms for this example. The values of U_{iso} are a reasonable guess for this material and the values of FRAC for atoms 2-5 are also reasonable guesses for the distribution of iron and aluminum between the two sites. The full atom editing menu is shown below.

```
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

Because there are atoms that occupy the same site, their atom parameters must be constrained to shift together during least squares refinement. In this case the two sets of atom locations are fixed by symmetry so constraints need only be applied to the thermal parameters and the atom fractions. These constraints are not needed for the initial least squares refinements, but they will be needed for later stages of the refinement and it is convenient to enter them now while you are thinking about them. Enter **'K'** to edit atom constraints.

```
Editing atomic constraints:
Enter atom parameter linear constraint editing command (<?>,D,I,L,X) >
```

You will need to enter four sets of constraints, two for U_{iso} and two for FRAC on each of the two sites. First enter those for U_{iso}; enter **'I'** to insert the first one.

```
Phase no., var_name, atom no. & coeff.?(<CR> to terminate) >
```

Enter **'1 UISO 2 1'** for the first term and **'1 UISO 3 1'** for the second. Then enter **'CR'** to complete the first constraint. This will define U_{iso} for atoms 2 and 3 as one variable in **GENLES**. In a similar fashion enter the constraint on U_{iso} for atoms 4 and 5; this will make U_{iso} for these atoms another single variable in **GENLES**.

The constraints on FRAC for these atoms are set so that both sites remain full regardless how the individual values of FRAC change. For example, if FRAC for atom 2 increases the constraint should make FRAC for atom 3 decrease by an identical amount. The same idea applies to the values of FRAC for atoms 4 and 5. Enter **'I'** for the first one.

```
Phase no., var_name, atom no. & coeff.?(<CR> to terminate) >
```

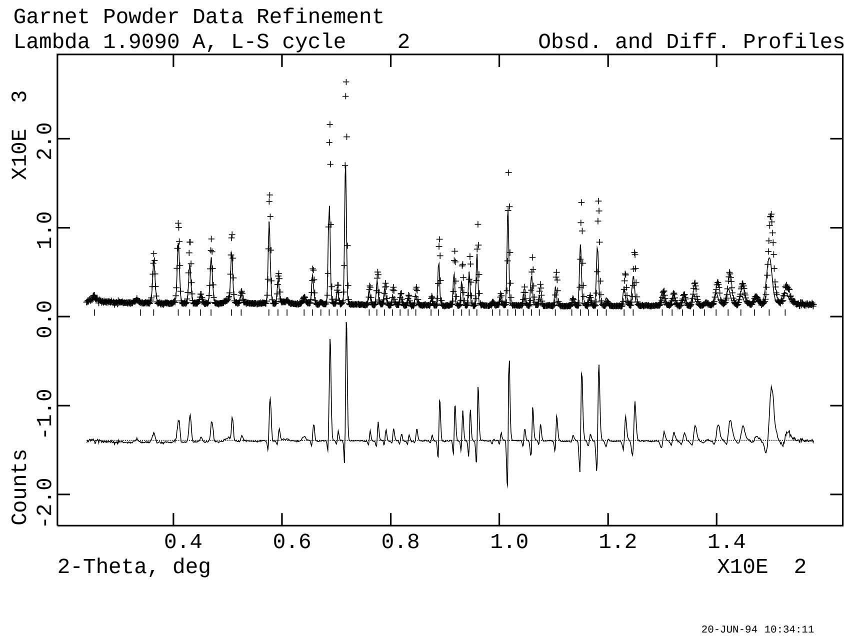
Enter **'1 FRAC 2 1'** followed by **'1 FRAC 3 -1'** and a **'CR'** for the first FRAC constraint. This means that FRAC for atom 3 will decrease if FRAC for atom 2 increases and visa-versa. In a similar fashion enter a constraint on FRAC for atoms 4 and 5; remember to change the sign of the coefficient for the second term. When you are done there should be four constraints for the two pairs of atoms. Enter **'L'** to list them.

```
Linear atomic constraint no.    1
Phase,parm.,atom,coeff. =  1  UISO   2    1.0000
Phase,parm.,atom,coeff. =  1  UISO   3    1.0000
Linear atomic constraint no.    2
Phase,parm.,atom,coeff. =  1  UISO   4    1.0000
Phase,parm.,atom,coeff. =  1  UISO   5    1.0000
Linear atomic constraint no.    3
Phase,parm.,atom,coeff. =  1  FRAC   2    1.0000
Phase,parm.,atom,coeff. =  1  FRAC   3   -1.0000
Linear atomic constraint no.    4
Phase,parm.,atom,coeff. =  1  FRAC   4    1.0000
Phase,parm.,atom,coeff. =  1  FRAC   5   -1.0000
Enter atom parameter linear constraint editing command (<?>,D,I,L,X) >
```

Enter **'X X X'** to return to the main **EXPEDT** menu. You may now exit from **EXPEDT** by entering **'X'**.

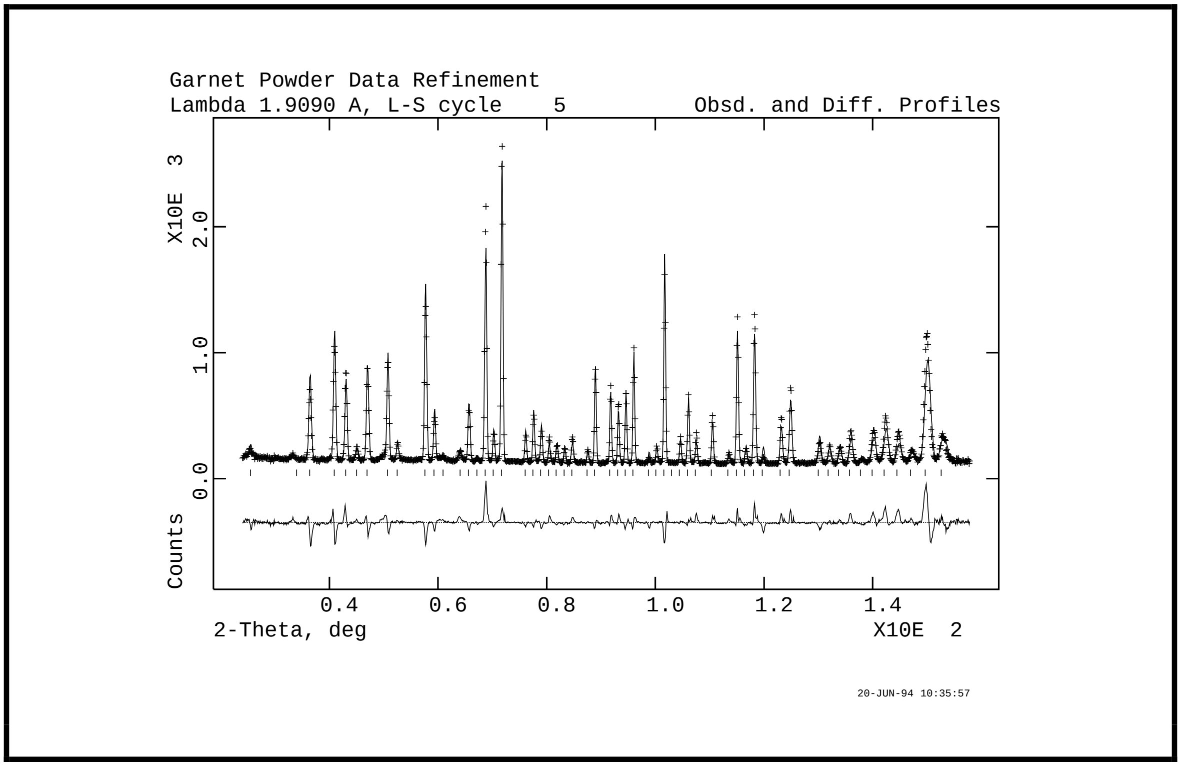
Powder Data Preparation and Refinement

You are now ready to run two batch jobs. The first will run **POWPREF** and the second will run **GENLES**. These may be submitted individually but **POWPREF** must finish before you submit **GENLES**. Alternatively, on a VMS system you may submit them both to be run sequentially by entering **'POWPREF GENLES'** at the **GSAS** command prompt. You will be asked a pair of questions about each of the two batch jobs to be run. By this means a set of up to seven batch jobs may be submitted and the list can have duplicate programs. This option is not available on the UNIX versions of **GSAS**. After both jobs finish use **POWPLOT** to look at the results of the refinement.



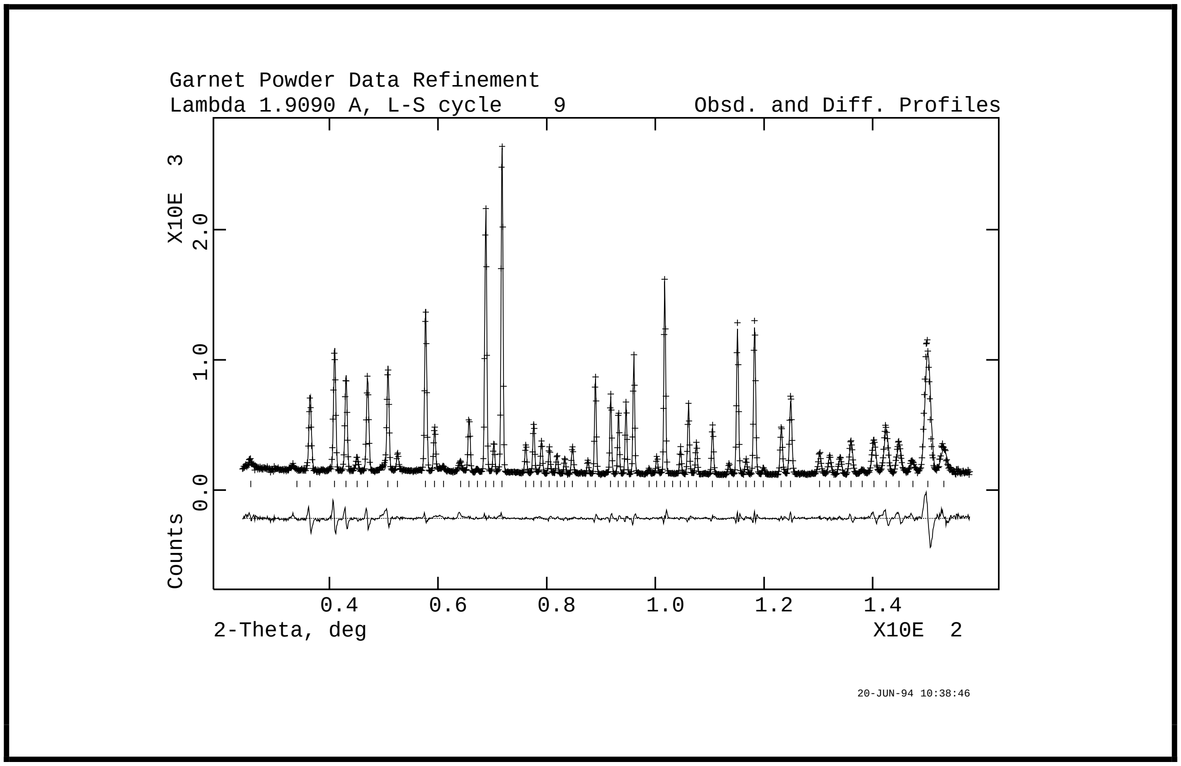
As you can see the fit at this point is quite poor and more parameters need to be varied before the fit will improve. Close examination of the difference curve indicates that a lot of the error arises from lattice parameter and zero point. The list output shows that while the refinement converged rapidly, the residuals are quite high (~32%). You should set the appropriate refinement flags (zero and lattice parameters) for the next least squares run. Because the previous least squares did not modify the peak positions, it is not necessary to rerun **POWPREF** before the next run of **GENLES**.

After refinement of the lattice parameter and zero point to convergence, the residuals are 9-10% and the fit to the pattern is considerably improved.

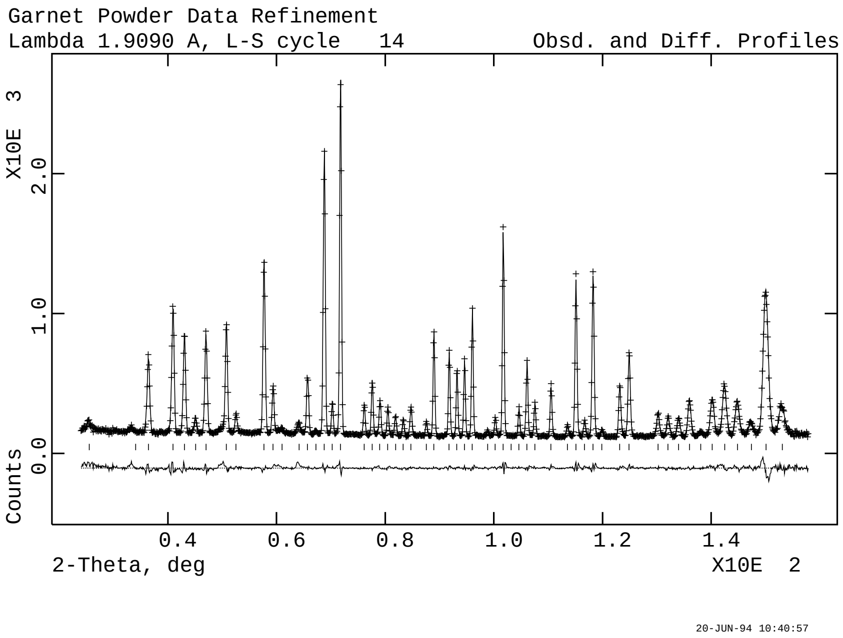


Examination of the fit seems to indicate that the major differences are related to structural details and profile shapes. Notice that several peaks have the wrong calculated intensity; this indicates a structural problem. In this case it is probably a combination of positional errors for the oxygen atom, atom fractions for the iron/aluminum sites and thermal parameters for all atoms. We suggest that you refine all these first; you should also increase the maximum number of L-S cycles to five. The atom constraints which were entered earlier are needed here to control the refinement of the atom fractions and thermal parameters for the Fe/Al atoms. The other major difference is that the peak shapes are in error; especially at the ends of the pattern. Refinement of the profile coefficients will be necessary; this should be done after the atom refinement has converged. In this case you need to run both **POWPREF** and **GENLES** because the previous refinement moved the peak positions relative to the pattern.

After refinement of the atomic parameters the residuals are much lower (5-7%) and the profile fit is much better.



As you can see all the peak intensity errors have disappeared leaving only the peak shape errors at the ends of the pattern. Now refine the first four (U, V, W and asym) peak shape coefficients. You will also want to increase the number of background coefficients to six. Again run both **POWPREF** and **GENLES**. After this refinement has converged the profile should look like the next plot.



Clearly there are no longer any major differences between the observed and calculated profiles; the residuals are 3-5%. An exception is the large peak at ~150˚; the remaining residual is probably due to an incomplete peak shape model. This is suggested by the shape of the difference curve. You may add additional parameters for anisotropic thermal motion and more background and profile coefficients; the improvement will be slight. If you do decide to refine the anisotropic thermal parameters for the Fe/Al sites, the constraints will have to be changed to include those for each u_{ij} on each site. For the final refinement, you should rerun **POWPREF** before the final run of **GENLES**. This assures that the peak positions and widths are correctly calculated.

Fourier Setup and Calculations

Before a Fourier calculation can be performed from powder data, a set of "observed" structure factors must be available. This is done in **GSAS** by the least squares program **GENLES** by dividing up the observed profile intensity above background among the contributing reflections according to their calculated intensity. Thus the "observed" structure factors are biased by the model used in the least squares. Nonetheless, these structure factors can contain sufficient information to find, for example, atoms that are missing from the structure. The appropriate option is set from the least squares controls menu in **EXPEDT**.

```
Maximum number of cycles is   5
Enter L-S control editing option (<?>,C,E,L,P,X) >
```

Enter **'E'** to select the F_o extraction option. As this is selectable for individual histograms, **EXPEDT** requests the histogram number you wish to extract F_o's from.

```
 Enter histogram number >
```

Enter **'1'** to select the histogram in the garnet example; the default extraction information for that histogram is presented next.

```
New histogram selected

Histogram no.   1 Bank no.  1 Lambda =  1.90900
Title: Y3FE2(ALO4)3 RT 1.909
Histogram will be used in least-squares
Fo's will not be extracted from this histogram
Experiment phase flags:           1    0    0    0    0    0    0    0    0
Histogram Fo extraction flags :   0    0    0    0    0    0    0    0    0
0 for normal 1 for LeBail method
Fo extraction flag editing options - (<?>,C,E,H,L,N,X) >
```

There are two techniques available in **GSAS** for the extraction of F_O's from powder data. The "normal" method apportions the observed Bragg intensity above background according to the portion of the total calculated intensity contributed by each reflection to give a set of "observed" structure factors with phases. Thus, the extraction is biased by the calculated structure factors and hence the structure model. Nonetheless, there is sufficient information in the extracted F_O's so that meaningful difference Fourier maps can be produced to locate missing atoms, etc. The "le Bail" method begins with a set of calculated structure factors based on a partial or dummy structure to obtain an initial set of F_O's. On subsequent least-squares cycles the set of F_O's extracted from one cycle are used as the F_C's for the next. In this way a set of F_O magnitudes (i.e. no phases) can be obtained even in the absence of a structural model. They can be used to produce Patterson maps or passed on to a direct methods package (SHELX, MULTAN, etc.) for structure solution. The le Bail method can also be used to fit sets of reflections from second phases, sample holders, chambers or other sources that appear as unwanted additions to the pattern. Thus, the extraction method can be selected individually for each phase. The default flags are set so that no extraction will occur and that "normal" is the default method. Enter '**CR**' to see the help listing.

```
Histogram phase flag editing options
 <?> - Type this help listing
 C   - Change Fo extraction method flags
 E   - Toggle main Fo extraction flag
 H m - Select new histogram "m"
 L   - List the current Fo extraction flags
 N   - Select next histogram
 X   - Exit to least squares control editing menu
Fo extraction flag editing options - (<?>,C,E,H,L,N,X) >
```

Select option **'E'** to set calculation of observed structure factors by the "normal" method. This option increases the computation time for a cycle of least squares by 10-20%, thus it should be only used when needed. A message will appear indicating that extraction is to be done.

```
Fo's will be extracted from this histogram
Fo extraction flag editing options - (<?>,C,E,H,L,N,X) >
```

You are now done setting the extraction flag so enter **'X'** to return back to the least squares controls menu. You may also wish to set the number of cycles (**'C'** option) to zero to reduce the computation time; the structure factor and profile calculations will be made but no least squares matrix will be generated. Now return to the main **EXPEDT** menu.

```
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

The next step is to set the Fourier controls; this is a main **EXPEDT** option. Enter **'F'** to select this option.

```
Enter desired map (<?>,DELF,FCLC,FOBS,PTSN,DPTS,EXIT) >
```

The available Fourier calculations include Patterson (**'PTSN'**), difference Patterson (**'DPTS**)', observed Fourier (**'FOBS'**), difference Fourier (**'DELF'**) and calculated Fourier (**'FCLC'**) maps. The first two can be calculated from le Bail extracted intensities; the others require F_O values extracted by the "normal" method. We want you to calculate an observed Fourier map for the garnet so enter **'FOBS'**.

```
Enter section desired (X,Y,Z) >
```

You are now requested to indicate the axis that is to vary from section to section in the Fourier calculation. In the case of garnet, which is cubic, there is no preferred direction so enter **'X'**. If you anticipate that there will be fewer points to be calculated along a particular axis then choose that axis; the calculation will use less computer time than the other choices.

```
Do you wish to specify individual map steps for each axis (Y/<N>)? >
```

Generally, the grid size for a Fourier map should be the same along the three axes; only in special cases might you need different size steps. Respond with **'CR'** to select a single grid size.

```
Current overall map step size is  0.2000 A
Enter new overall map step size in Angstroms >
```

This is a reasonable map step size so enter **'/'**. This choice ensures that the contouring routines **FORPLOT** and **PLOTTER** will draw sensible contours without consuming too much computer time. The next listing shows the chosen step size and number of steps for each cell edge. The step sizes are adjusted so that special sections (1/4, 1/3, 1/2 etc.) are explicitly included according to the cell symmetry.

```
The a-axis is  12.188955 A
The new del-x is  0.2031 A
The cell will be divided into   60 points along x
The b-axis is  12.188955 A
The new del-y is  0.2031 A
The cell will be divided into   60 points along y
The c-axis is  12.188955 A
The new del-z is  0.2031 A
The cell will be divided into   60 points along z
Old x limits are  0.0000 to  0.0000
Enter minimum and maximum values of x in fractions of the cell edge >
```

The next step is to set the axes limits for the Fourier calculation. The old x limits are clearly wrong. Reference to "International Tables for Crystallography, Vol. A" suggests that the limits on the x-axis for this space group are -1/8 to 1/8. Enter **'-1/8 1/8'**.

```
New x limits are -0.1250 to  0.1250
Old y limits are  0.0000 to  0.0000
Enter minimum and maximum values of y in fractions of the cell edge >
```

The new limits for x are shown; they are set to be on a grid point. As was for x the old y limits are wrong; the suggested range is also -1/8 to 1/8. Enter **'-1/8 1/8'.**

```
New y limits are -0.1250 to  0.1250
Old z limits are  0.0000 to  0.0000
Enter minimum and maximum values of z in fractions of the cell edge >
```

The new limits for y are shown; again they are on a grid point. The z limits should be 0 to 1/4. Enter **'0 1/4'.**

```
New z limits are  0.0000 to  0.2500
At least one asymmetric part of the unit cell is included in the Fourier.
Enter new list of histogram numbers in the order you wish them to be read.
The last occurrence of a reflection will be used.
Include histogram (0 to terminate list) >
```

The new z limits are shown. The message indicates that the volume you have selected contains at least a complete unique part of the unit cell. Next you have to indicate which histograms contribute reflections to the calculation. In case of duplicate reflections between histograms, the last one found will be used in the Fourier calculation. Thus the numerical order of the histograms entered here may be important. For this example there is only one histogram so enter **'1 0'** to include it and terminate the list.

```
Enter FOURIER map calculation option (<?>,A,D,E,F,H,I,L,M,P,R,S,T,W,X) >
```

This is the main Fourier control menu; enter **'CR'** to see the help listing.

```
The FOURIER control data edit options are
<?> - Type this help listing
 A  - Add another map to the set to be calculated
 D  - Change minimum reflection D-spacing for this phase
 E  - Erase a map from the set to be calculated
 F  - Edit phase composition
 H  - Select histograms to include in the map
 I  - Enter new map intervals
 L  - List the current controls
 M  - Select map type to be computed
 P  - Select phase (only one can be processed by FOURIER
 R  - Enter new unit cell limits for the map
 S  - Change the sections control
 T  - Change the experiment title
 W  - Change the map listing options
 X  - Exit to EXPEDT main menu
Enter FOURIER map calculation option (<?>,A,D,E,F,H,I,L,M,P,R,S,T,W,X) >
```

All of the items you have just entered can be now edited separately from this menu. Enter **'L'** to list the current settings.

```
Current Fourier map options for phase 1 are:
Calculate a FOBS map
Do not generate a map listing
Calculate sections at constant X
Divide the cell into   60 points along x
The x interval is 0.2031 A
The range is -0.1250 to  0.1250
Divide the cell into   60 points along y
The y interval is 0.2031 A
The range is -0.1250 to  0.1250
Divide the cell into   60 points along z
The z interval is 0.2031 A
The range is  0.0000 to  0.2500
At least one asymmetric part of the unit cell is included in the Fourier.
There are  1 histograms
The histogram type flags are
 1 PNC
 1 of them are to be used
The ones to be used are:
    1
F000 is  98.071
Enter FOURIER map calculation option (<?>,A,D,E,F,H,I,L,M,P,R,S,T,W,X) >
```

You are all finished with **EXPEDT** so return to the main **GSAS** prompt by entering **'X'** a sufficient number times.

The next section of this manual describes the map display program **FORPLOT** but first you need to extract structure factors and calculate the Fourier. At the **GSAS** prompt on a VMS system enter **'GENLES FOURIER'** and respond to the two pairs of batch job questions. Both runs are relatively short so choose the appropriate queue. Two batch jobs will be submitted to perform the required calculations; after they finish continue with the exercise. The operation is essentially the same for UNIX except that **GENLES** and **FOURIER** are run sequentially.

Fourier Map Display

In this section you will run the Fourier display program **FORPLOT**. It is capable of displaying single slices of the density map calculated by **FOURIER** in any orientation and over any range. A slice is produced by 8 point interpolation for each point in a grid covering the slice area to the computed map and uses symmetry operations to complete the coverage. The plots are always square and are contoured with levels of your choosing. The area covered by the slice is limited by computer memory and is also related to the fineness of the grid. Successive plots may be generated by incremental displacement and rotation from a reference position. This exercise will demonstrate some of these facilities.

To start the program type **'FORPLOT'** at the main **GSAS** prompt; the following will be displayed.

```
               |-----------------------------------------------|
               |         Program FORPLOT Version 6.25          |
               | Crystal structure Fourier map drawing program |
               |    Distributed on TEST Vers. 20-JUN-1994      |
               |-----------------------------------------------|
       |---------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele           |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
       |                                                               |
       | Copyright, 1994, The Regents of the University of California. |
       |---------------------------------------------------------------|

Enter terminal type (<?>,A,B,C,D,E,F,G,H,Z) >
```

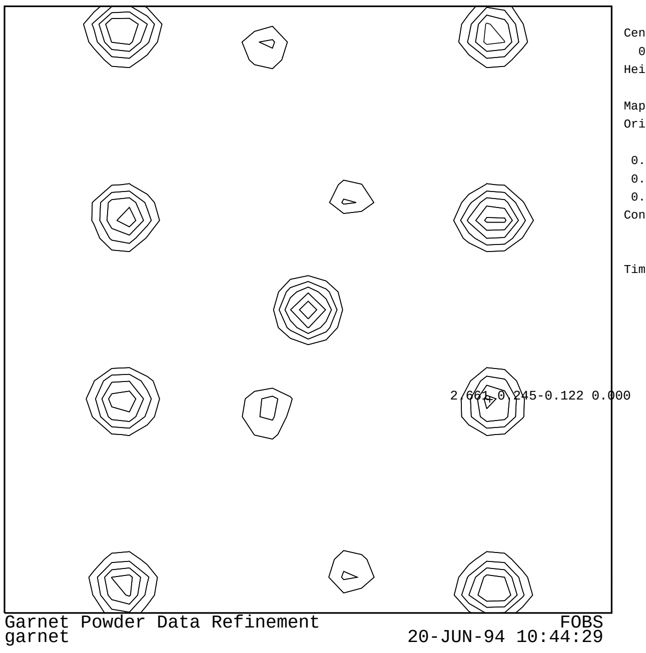
As in the earlier exercises with **EXPEDT** and **POWPLOT**, you need to identify the type of graphics terminal you are now using. Enter the appropriate letter. **FORPLOT** will read the map file output by **FOURIER** and show you a summary of what it found as well as the default plotting parameters.

```
A FOBS file has been opened
Problem title: Garnet Powder Data Refinement
Phase name: garnet
Map parameters:
Map X axis divided into   60 steps, from   -8 and covering   17 steps
Map Y axis divided into   60 steps, from   -8 and covering   17 steps
Map Z axis divided into   60 steps, from    0 and covering   16 steps
Map scaling factor  1.E+00
Rescaled rho limits from  -0.59 to   3.19
There were   4624 map elements stored
The map values range from   -0.59 to   3.19 with a scaling factor of  1.E+00
  5 contours will be drawn between rho =   0.00 and   3.19
with an interval of   0.53
Contours will be drawn at:
  0.53  1.06  1.59  2.12  2.65
The map center is at    0.00000   0.00000   0.00000
The map orientation vectors are:
U =    1.00000   0.00000   0.00000
V =    0.00000   1.00000   0.00000
Plot axes to crystal transformation matrix:
   0.082041    0.000000    0.000000
   0.000000    0.082041    0.000000
   0.000000    0.000000    0.082041

Height of section above center is   0.000 A
The map size - center to edge is   5.00 A
The map grid interval is 0.300 A
Enter FORPLOT command (<?>,A,C,D,G,F,H,I,L,M,N,O,P,Q,R,S,T,V) >
```

The first few lines indicate the step sizes and ranges for the Fourier calculations and show the number of elements in the map. The rest of the display shows the default settings. **FORPLOT** has selected 5 contours which are to be drawn at equal intervals between zero and the maximum map density. The default orientation is with the crystallographic *a*-axis horizontal, the *b*-axis up the screen and the *c*-axis out of the picture towards you. In this case they are orthogonal axes. The columns of the transformation matrix indicate the crystallographic real space vectors that are horizontal, vertical and normal to the screen; in this case 100, 010 and 001, respectively. Note that the menu is quite extensive, type **'CR'** to see the help listing.

```
FORPLOT commands:
 <?>   - Type this help listing
 A     - Define map center and orientation by entering 3 or 4 atom seq. numbers
 C c   - Set map center
 D     - Set atom labeling limit
 F     - Read a different Fourier map
 G g   - Set grid interval "g" in A (default = .3)
 H h   - Set height "h" of section above center in A
 I v   - Select contour interval in rho "v"
 L     - List current settings
 M v   - Select minimum rho value "v" (default = 0.0)
 N n   - Select number of contours "n" and assign their values
 P     - Plot map
 Q     - Quit FORPLOT
 R a r - Enter axis (x,y,or z) and angle for rotation of current drawing
 S s   - Set map size - center to edge (default = 5.0 A)
 T x y z  - Display rho at "x,y,z"
 V u v - Set map orientation vectors "u" and "v" (Enter 6 values)
         Map horizontal is u and normal is uxv
Enter FORPLOT command (<?>,A,C,D,G,F,H,I,L,M,N,O,P,Q,R,S,T,V) >
```

There are several types of commands for **FORPLOT**. One set controls the contours ('**G**', '**I**', '**N**' and '**M**'), another the map orientation and position ('**A**', '**C**', '**H**', '**R**' and '**V**') and the rest provide information. To see the default plot type '**P**' and the contoured plot will immediately follow.



```
Center of reference
  0.000  0.000  0.000
Height above center
    0.000 A
Map size  10.000 A
Orientation matrix
    U      V     UXV
 0.0820 0.0000 0.0000
 0.0000 0.0820 0.0000
 0.0000 0.0000 0.0820
Contours are drawn at
   0.53   1.06   1.59
   2.12   2.65
Times   1.
```

```
Garnet Powder Data Refinement                  FOBS
garnet                            20-JUN-94 10:44:29
```

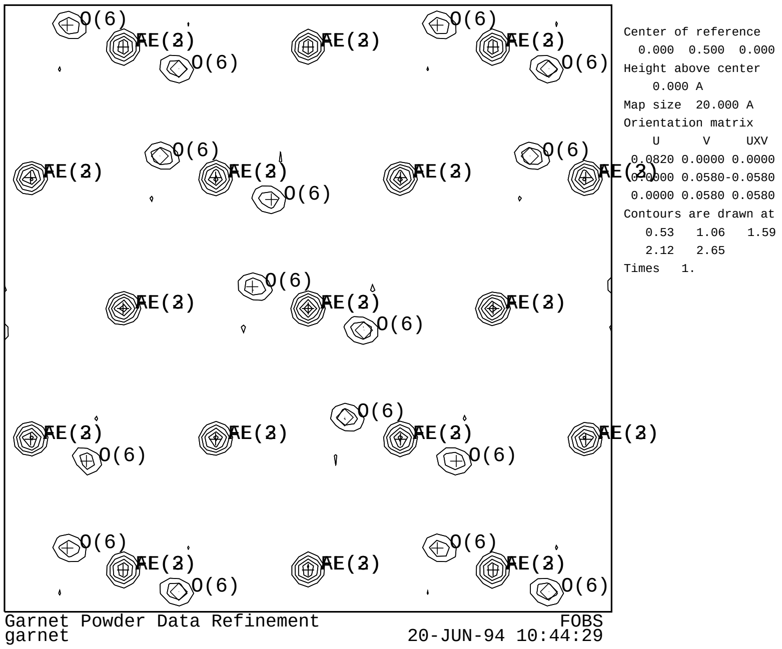
This is a 10 X 10Å *ab*-section centered at 0,0,0 looking down the *c*-axis of the garnet cell. The peak in the center is the first Fe/Al atom, the smaller peaks nearby are close to the O atom positions and the intermediate peaks to the right and left are Y atoms. A graphics cursor and a menu also appears on the plot. To move the cursor push the arrow keys (or mouse) until it is positioned where you want. The picture in this manual has the cursor placed on the peak with the numbers nearby. Move the cursor to that peak and type **'W'** to show its crystallographic coordinates. They are printed to the right. Then type **'H'** to show the density; it is printed to the left. The **'C'** option allows you to set the map center for the next picture. To exit the cursor mode and return to the main **FORPLOT** menu, type **'X'**.

```
Enter FORPLOT command (<?>,A,C,D,G,F,H,I,L,M,N,O,P,Q,R,S,T,V) >
```

The next plot we want you to try is a view with the *a*-axis horizontal and the 110 real axis vertical; this will give a view down the real space 0-11 vector. Enter **'V 1 0 0 0 1 1'**; this will set the U and V vectors. **FORPLOT** will then display the new orientation matrix.

```
New grid to crystal transformation matrix:
   0.08204   0.00000   0.00000
   0.00000   0.05801  -0.05801
   0.00000   0.05801   0.05801
Enter FORPLOT command (<?>,A,C,D,G,F,H,I,L,M,N,O,P,Q,R,S,T,V) >
```

We want the center of the plot to be at 0,1/2,0 and span twice the range as the previous plot. We also want all atoms that fall within 0.5Å of the plot plane to be labeled. All these commands can be entered on one line so type **'C 0 1/2 0 S 10 D 0.5 P'**, the plot will immediately follow.



```
Center of reference
  0.000  0.500  0.000
Height above center
    0.000 A
Map size  20.000 A
Orientation matrix
    U      V     UXV
 0.0820 0.0000 0.0000
 0.0000 0.0580-0.0580
 0.0000 0.0580 0.0580
Contours are drawn at
   0.53   1.06   1.59
   2.12   2.65
Times   1.
```

```
Garnet Powder Data Refinement                    FOBS
garnet                              20-JUN-94 10:44:29
```

You may wish to explore this structure using some of the other options of **FORPLOT**. There are some precedence rules for the various options that you should be aware of. The **'R'** commands are cumulative, that is each rotation is applied to the previous orientation to give a new one. A **'V'** or **'A'** command starts a new orientation and wipes out the effect of any previous **'R'** commands. The height option **'H'** is only effective for the next plot to be drawn, after the plot is made the height is reset to zero. A new set of contours is only generated by the **'I'** and **'N'** options. Changing the minimum density with the **'M'** option will not generate extra contour levels until an **'I'** option is given, and **'M'** has no effect on the contour levels set with the **'N'** option..

Distance-Angle Setup and Calculations

There is a set of controls for a distance/angle calculation which are set to some default values. In this part of the exercise you will examine them. The editing of these controls is reached by the **'D'** option in the main **EXPEDT** menu.

```
Select editing option for Distance/angle calculation (<?>,A,D,P,T,X) >
```

This is the distance/angle editing main menu. Here you can completely define a known crystal structure; both phase and atom editing options are available. Enter **'?'** to see the help listing.

```
The available options are:
 <?> - Type this help listing
 A   - Edit atom parameters
 D   - Edit the distance/angle routine controls
 P   - Edit phase data - lattice & sp. group
 T   - Change the experiment title
 X   - Return to main EXPEDT menu
Select editing option for Distance/angle calculation (<?>,A,D,P,T,X) >
```

Since you are interested in distances and angles for the refined structure of yttrium-iron garnet enter **'D'** to examine the controls.

```
Current Distance and Angle options for phase  1 are:
Calculate distances based on atom type limits
Calculate angles based on atom type limits
Atom type   Dist. radii   Angle radii
  Y            2.00        1.80
  FE           1.47        1.27
  AL           1.60        1.43
  O            1.09        0.89
Do not include any Fourier map peaks
Enter DISAGL control data edit option (<?>,C,D,F,L,N,O,X) >
```

The default setup for a distance/angle calculation is shown. The atom radii were obtained from the atom data file and provide a reasonable starting point for upper limits for bond distance and angle calculations. These can be changed with the **'C'** option. You also have the choice of using overall limits for both distance and angle calculations. This choice is also made with the **'C'** option. Enter **'?'** to see the help listing.

```
The DISAGL control data edit options are
 <?>  - Type this help listing
 C   - Change distance limit type and values
 D   - Delete calculation of distances for this phase
 F   - Change the Fourier peak inclusion option
 L   - List the current controls
 N n - Process phase "n"
 O   - Select a new output option
 X   - Exit to DISAGL editing main menu
Enter DISAGL control data edit option (<?>,C,D,F,L,N,O,X) >
```

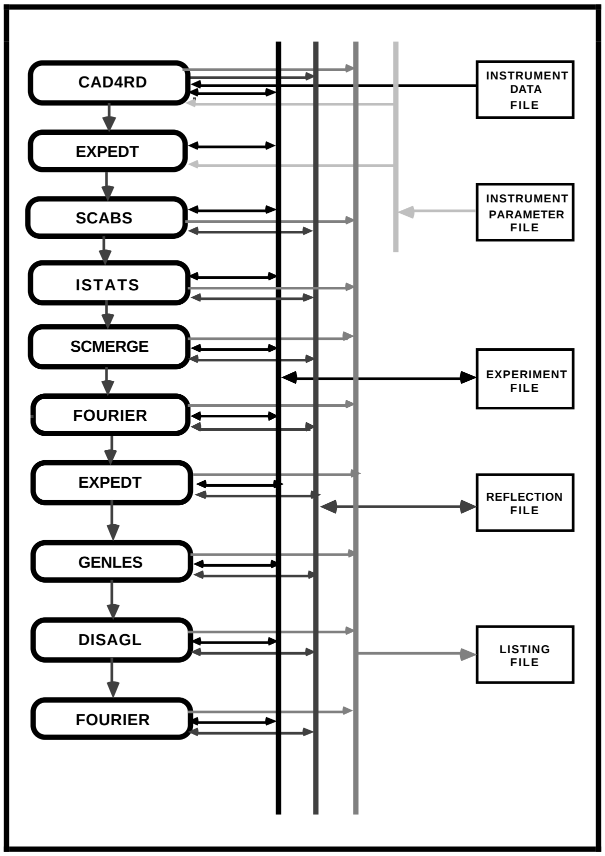
Since the default selections for the controls are reasonable for a distance/angle calculation enter **'X'** a sufficient number of times to exit **EXPEDT**.

To run the distance/angle program enter **'DISAGL'** at the **GSAS** prompt and respond to the two batch run questions. This calculation is quite rapid so select a fast batch queue. The output will be appended to the list file and can be examined after the job completes.

Single Crystal X-ray Data Exercise

As an introduction to the use of **GSAS** to process single crystal data, we present first a flow diagram for the run which we want you to work through. This is given in the box below.

We have prepared an exercise to acquaint you with using **GSAS** for single crystal data analysis. The example which we are using is oxonium hexafluoroantimonate, $(H_3O)^+(SbF_6)^-$. This structure has been published in *Acta Crystallographica* **B**. The compound is cubic and the space group is either Ia3 or $I2_13$. The lattice constant is 10.120(7) and there are eight formula units per unit cell. The raw data for this exercise was collected on a Enraf-Nonius CAD4 single crystal diffractometer.



CAD4 Data Setup

To begin set the default directory to where you wish to run this exercise and enter **'GSAS OXONIUM'** to start the **GSAS** command file and set the experiment name to 'OXONIUM' which is the name we have chosen for this exercise.

```
                             Welcome to GSAS
                  The General Structure Analysis System

       Current listing output page length is 60 lines
       Default for running Least-squares and other long jobs is ONLINE
       Enter a ? or a simply a <CR> for information on available commands

%SYSTEM-W-NOSUCHFILE, no such file
 \OXONIUM.EXP\
  The experiment is OXONIUM  creation date =
MIST::GSAS Command? >
```

As with the powder exercises the error message informs you that these is no experiment file for OXONIUM, you will create it in a moment. In the first part of this exercise you create the experiment file at the same time the diffraction data is read. Enter**'CAD4RD'** to begin and you will get the first prompt .

```
Experiment - OXONIUM - was not found.
Do you wish to create it (Y/<N>)? >
```

You want to create the file OXONIUM.EXP, so enter **'Y'** and you will get the next prompt. After it is created you should not see this prompt at the beginning of **CAD4RD** or **EXPEDT** unless you are inadvertently in the wrong directory or have the wrong experiment name.

```
The new experiment - OXONIUM - has been created.
 Enter a title for this experiment
  >
```

Give the experiment a title, '**Single Crystal Exercise'** might be an appropriate one. At this point you will see the program banner and the next prompt.

```
           |------------------------------------------------------|
           |             Program CAD4RD Version 6.14              |
           |         Convert CAD4 data to a standard form         |
           | Modified by James Fait, University of Calgary Apr 89 |
           |              Modified by ACL Feb, Apr 90             |
           |       Distributed on TEST Vers. 20-JUN-1994          |
           |------------------------------------------------------|
       |---------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele           |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
       |                                                               |
       | Copyright, 1994, The Regents of the University of California. |
       |---------------------------------------------------------------|

Enter Single Crystal instrument parameter file name (<?>,$,QUIT)
  >
```

The file **'GSAS_EXERCISES:INSTPARM.CAD4'** (for UNIX use **'/usr/gsas/INSTPARM.CAD4'**) is the instrument parameter file for the CAD4. It contains information that characterizes the Enraf-Nonius CAD4 diffractometer including the relationship between the goniometer and the 'laboratory coordinate system' as well as the sense of rotation and zero positions of the goniometer circles. It also has attenuator data and a nominal wavelength. Notice that the possibility of executing system commands is available here (the '**$'** command).

```
Enter single crystal data file name (<?>,$,QUIT)
  >
```

The next prompt is for the CAD4 data file which contains both the results of the lattice parameter and orientation matrix determination as well as the entire data acquisition results. Enter **'GSAS_EXERCISES:OXONIUM.DAT'** (or **'/usr/gsas/gsas_exercises/OXONIUM.DAT'** for UNIX) so that this information can be introduced to **GSAS**. Again system commands can be used to search for it.

```
First record:  21     1KENT'S H3O+SBF5- LOW TEMP -50C       173 4.0 1.3 5.9
Is this the correct file (<Y>/N/Q)? >
```

The first record on the CAD4 data file is reproduced here and you are given the opportunity to reject it. This is the correct file so enter **'CR'** to accept it.

```
There is no phase information present
Enter identifying name for new phase number 1.
  >
```

We need to enter some phase information as a first step in this process. The first request is for a name of this phase, **'(H3O)+(SbF6)-'** or something else appropriate will do. You will then be asked for further information about this phase.

```
No space group information found
Enter space group symbol (ex:  P n a 21, P 42/n c m, R -3 c, P 42/m,
R -3 m R for rhombohedral setting) >
```

First you need the space group. This data set was collected in a way that places the antimony atom on the intersection of mirrors *bca* at 1/4,1/4,1/4 in Ia3; this is the 8b site. The 8a site at 0,0,0 is taken by the oxygen atom. If you use the alternate name for this space group, Ib3, then these two sites are interchanged so that the antimony atom is at the origin and the oxygen atom at 1/4,1/4,1/4. We have assumed that the alternate choice is used so enter **'I B 3'** as the space group and you will get the following screen..

```
Space group I b 3
The lattice is centric  I-centered cubic         Laue symmetry m 3
 Multiplicity of a general site is  48
 The symmetry of the point 0,0,0 contains 1bar

The equivalent positions are:

 ( 1)     X      Y      Z   ( 2)     Z      X      Y   ( 3)     Y      Z      X
 ( 4)     X  1/2+Y  1/2-Z   ( 5) 1/2-Z      X  1/2+Y   ( 6) 1/2+Y  1/2-Z      X
 ( 7) 1/2-Z  1/2+X     -Y   ( 8)    -Y  1/2-Z  1/2+X   ( 9) 1/2+Y     -Z  1/2-X
 (10) 1/2-X  1/2+Y     -Z   (11)    -Z  1/2-X  1/2+Y   (12) 1/2+X     -Y  1/2-Z

Enter real lattice parameters (Angstroms)
Enter a >
```

As was the case for the powder examples **GSAS** determines that only the *a* lattice parameter is needed for this cubic cell. Enter **'10.12'** and a full list of the lattice constants and calculated cell volume is shown next.

```
Lattice parameters are
    a,b,c  = 10.120001 10.120001 10.120001
    angles =    90.000    90.000    90.000
    volume =  1036.434
Lattice symmetry is cubic
Space group symmetry is cubic
Enter phase edit command(<?>,$,D,E,F,M,I,L,S,X) >
```

Enter **'?'** or **'CR'** to see the options available from this menu.

```
Phase editing commands:
 <?> - Type this help listing
 $   - Enter DCL command
 D n - Delete all data for phase "n"
 E n - Edit phase data for phase "n"
 F n - Enter unit cell contents data for phase "n"
 I   - Insert new phase
 M n - Toggle magnetic flag for phase "n"
 L   - List phase names
 S n - Enter unit cell sigmas
 X   - Exit to EXPEDT main menu
At least one phase must be defined before leaving this menu
Enter phase edit command(<?>,$,D,E,F,M,I,L,S,X) >
```

The CAD4 data file does not contain the error information on the lattice constants so we should enter σ_a into the data file. To do this select option **'S'** from this menu.

```
All sigmas for lattice parameters = 0.00
Enter real lattice parameter Sigmas (Angstroms & degrees)
       ( enter / if current values are OK )
Enter Sigma(a) >
```

As with the lattice parameter input, only the error for the *a* lattice parameter is needed for a cubic cell. Enter **'.007'** and the menu prompt for phase editing is shown.

```
Enter phase edit command(<?>,$,D,E,F,M,I,L,S,X) >
```

The next step is to enter the probable unit cell contents; these are required for the absorption calculation that will be run in a few moments. Enter **'F'**.

```
Unit cell contents not known
Enter unit cell composition edit command (<?>,$,C,E,F,L,X) >
```

You see a message that there is no information on the unit cell contents. To see the entries in this menu enter **'CR'**.

```
Unit cell composition editing commands:
 <?> - Type this help listing
 $   - Enter DCL command
 C   - Change unit cell composition
 E   - Edit unit cell composition data
 F   - Edit form factor information
 L   - List unit cell composition
 X   - Exit to phase editing menu
You are limited to 9 atom types for all phases
Enter unit cell composition edit command (<?>,$,C,E,F,L,X) >
```

You want to change the unit cell contents so enter **'C'**.

```
Enter atom type for type(1) (<CR> to quit) >
```

And now enter **'h 24 o 8 sb 8 f 48'** to define the contents of the unit cell.

```
Enter atom type for type(5) (<CR> to quit) >
```

The entry of chemical formula data is terminated with a blank line; enter **'CR'**. The program will next list the composition, calculated density, absorption coefficients and the F(000) structure factors for both x-rays and neutrons.

```
Unit cell contents for phase 1:
H          24.00 O          8.00 SB         8.00 F          48.00
F(000) neutrons =   27.30              Formula weight = 2038.09
F(000) xrays    =  927.94              The density is     3.265
  X-Ray Abs. Coefs. 1229.96 799.59 441.55  54.09  28.01
Neutron Abs. Coef.     0.48 +   0.48 Lambda
Enter unit cell composition edit command (<?>,$,C,E,F,L,X) >
```

You are finished here so exit formula editing by entering **'X'.**

```
Enter phase edit command(<?>,$,D,E,F,M,I,L,S,X) >
```

You are finished here so exit phase editing by entering **'X'**. You next have the opportunity to edit the information taken from both the CAD4 instrument parameter and data files.

```
Attenuator coefs. are
 1.0000 16.2300  1.0000  1.0000  1.0000  1.0000
Enter new values or a "/"
Enter ATNCOF(1) >
```

These six attenuator coefficients are taken from the instrument parameter file. They are correct for this data set so enter '/' to accept them. The program will next process the entire diffraction data file listing all lattice constant and orientation matrix changes which occurred during the data collection. Generally these changes are quite minor and can be ignored. The orientation information in the first one will automatically be accepted, but later ones will be presented for you to choose as to whether or not they are a better representation of the cell orientation than the first one.

```
 Nref =    0 Last iseq =    0   Exposure time =       0.  Lambda = 0.70930
 4.1278001E-02  9.7239995E-03  8.9162000E-02
-8.5389003E-02 -2.5436001E-02  4.2268999E-02
 2.7078001E-02 -9.4682999E-02 -2.5480001E-03
 Lattice constants are 10.1386 10.1502 10.1311   90.20   90.01   90.06
Phi =   64.58 Chi =   -91.29 Omega =   344.01

 Nref = 1460 Last iseq = 1926   Exposure time =   79282.  Lambda = 0.70930
 4.2096000E-02  9.4630001E-03  8.8886999E-02
-8.4546000E-02 -2.7169000E-02  4.3008000E-02
 2.8436000E-02 -9.4355002E-02 -3.5850001E-03
 Lattice constants are 10.1385 10.1375 10.1204   90.06   90.02   90.07
Phi =   64.16 Chi =   -92.02 Omega =   343.16
Save this orientation? (Y,<N>) >
```

The second orientation information is insufficiently different from the first one to warrant using, so don't save it; enter **'N'**.

```
There were  1497 reflections read
There were     2 standard reflections used
Do you wish to list the standard reflection data? (Y,<N>) >
```

You probably don't want to list the individual standard reflection data, so either enter**'CR'** or **'N'**. A summary of the intensity variation for the first standard is shown next.

```
Standard no.  1 is     0    4   -8
It was measured   12 times
Avg(i) = <WI>/<W> is            3520.67
Sigma(I)/Avg(I) =                0.0029
<abs(del(I))>/Avg(I) =           0.0280
rms(del(I))/Avg(I) =             0.0316
Sqrt(<I**2>-<I>**2)/<I> is       0.0316
Fitting of standards to a polynomial
Default number of terms (M) is:  2 The convergence criterion (C) is: 0.0100
Enter the initial number of terms (2-20), M >
```

The program will fit the intensity data to a polynomial series of the type

$$S_i = A + \sum_{n=1}^{M} B_n T_i^n$$

where M is the order of the polynomial and T is the x-ray exposure time for the crystal. The fitting routine will begin with the number of terms, M, entered and will fit the first standard until the convergence criterion is satisfied for that number of terms. Optionally, the routine will increase the number of terms and repeat the fitting until no further improvement can be obtained. The number of terms found for the first standard is then used for all subsequent standards. We shall start the polynomial fitting with two terms by entering**'2'**.

```
Enter the convergence criterion, C >
```

We will use the default convergence criterion of 0.01 by entering**'/'**.

```
Do you want to search for "best" number of terms (<Y>/N)? >
```

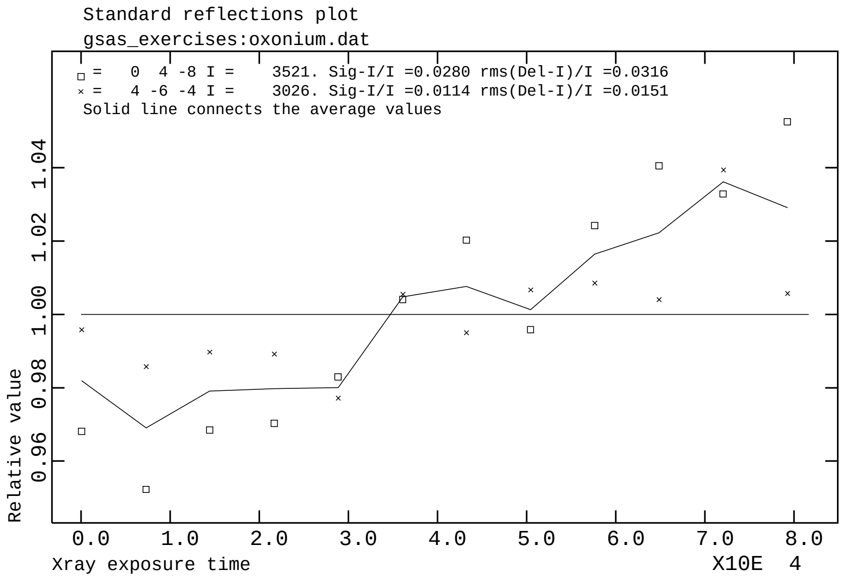
We want the program to search for the best number of terms so enter**'Y'**.

```
Number of terms  =  2 Convergence crit. =    0.01000
Sum of the squares of the residuals =    14690.6     M =  2
Sum of the squares of the residuals =    14280.9     M =  3
Sum of the squares of the residuals =    13175.3     M =  4
Sum of the squares of the residuals =    10963.7     M =  5
Sum of the squares of the residuals =    58296.0     M =  6

Coefficients of normalization polynomial
    1.00000       -0.169575         1.14993        -1.68633        0.800769
Errors for polynomial coefficients
   0.111243E-01    0.174331        0.779324         1.23120        0.628443
Polynomial evaluated at 0. and  81647.   1.00000   1.09480
rms(del(I))/<I> =                0.0476

Standard no.  2 is     4   -6   -4
It was measured   12 times
Avg(i) = <WI>/<W> is            3026.11
Sigma(I)/Avg(I) =                0.0031
<abs(del(I))>/Avg(I) =           0.0114
rms(del(I))/Avg(I) =             0.0151
Sqrt(<I**2>-<I>**2)/<I> is       0.0151
Number of terms  =  5 Convergence crit. =    0.01000
Sum of the squares of the residuals =    9414.70     M =  5

Coefficients of normalization polynomial
    1.00000       -0.385320E-01   -0.690919E-01    0.473014       -0.352103
Errors for polynomial coefficients
   0.116685E-01    0.182595        0.815299         1.28717        0.656700
Polynomial evaluated at 0. and  81647.   1.00000   1.01329
rms(del(I))/<I> =                0.0128
Plot the standards? (<N>/Y/X=EXIT) >
```

As you can see the program tried progressively more terms to fit the first standard. Introduction of the sixth term did not improve the fit so five terms was used for all fitting. The second standard was fit without any further requests from you. You next have the option to plot the standards. Enter **'Y'** for the first plot.

```
Enter terminal type (<?>,A,B,C,D,E,F,G,H,Z) >
```

Enter your terminal type letter followed by **'N'** to have no hardcopy plots. The first plot will immediately follow.



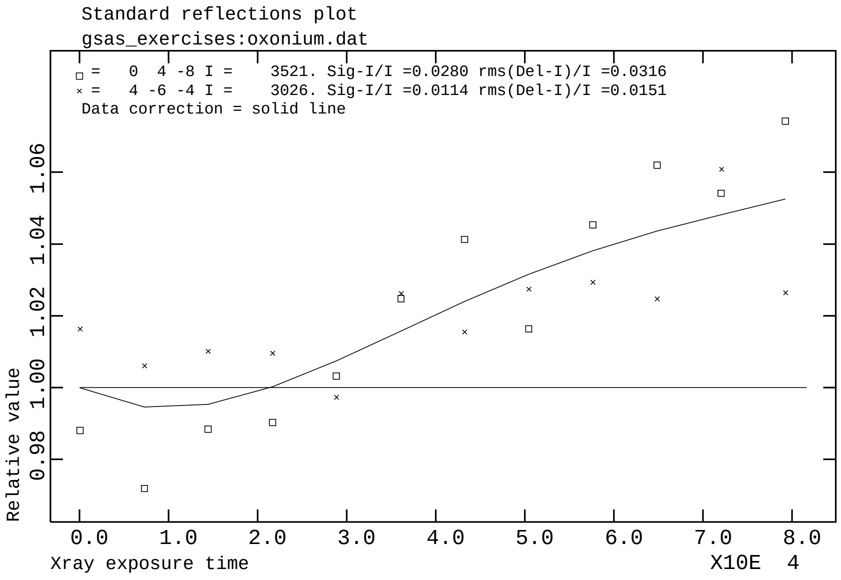
This plot shows the normalized intensities for both standards plotted as symbols along with their average as a solid line. Notice that in this case all three curves are similar so that an average correction is appropriate. On some terminals you need to enter **'CR'** to get the next prompt.

```
Use all of the standards? (<Y>,N) >
```

There is no reason why we should not use all standards measured, so enter **'Y'**.

```
Do you want to use polynomial fit? (<Y>,N) >
```

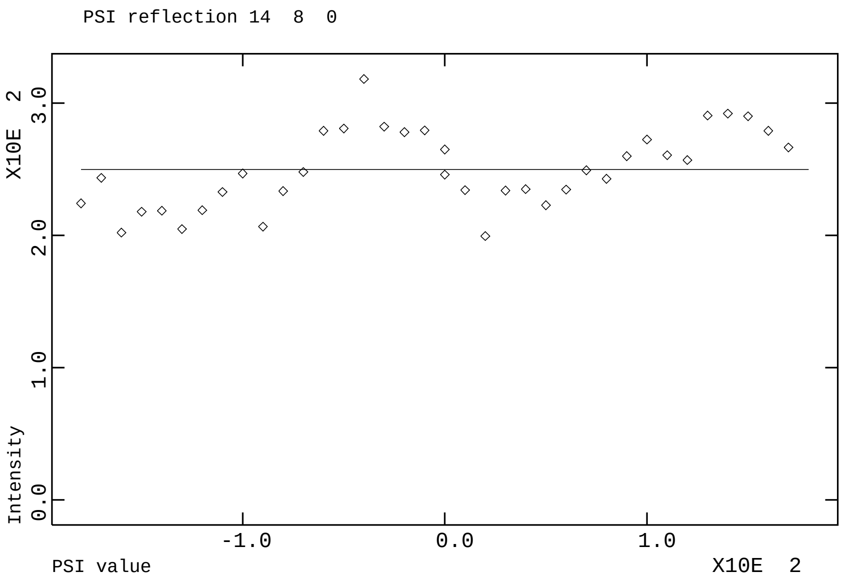
You now need to choose between using the results of the polynomial fit and a simple interpolation of the normalized average standard intensities. Generally the polynomial fit gives a better description of the intensity variations so enter **'Y'.** A plot of the standards and the polynomial fit will follow.



As you can see the five term polynomial fit gives a satisfactory description of the intensity variation. As above you may need to enter **'CR'** to get the next prompt.

```
Data will be corrected with the polynomial fit
Scan no. 1 for hkl  14  8  0 Avg-I      250. has  37 psi values starting at 1461
Do you want to plot this psi scan reflection (<Y>/N)? >
```

You are first advised that the polynomial fit to the standards will be used to correct the intensities. Then **CAD4RD** finds the first ψ-scan data and asks if you want to plot it. Enter **'Y'** and the plot will immediately follow.



This ψ-scan shows the typical sinusoidal variation due to absorption from a non-spherical crystal. If there was more than one ψ-scan reflection set they would be plotted in turn. As for the other plots enter '**CR**' if necessary to get the next prompt.

```
Enter the no. of the PSI reflection you want to use for absorption corrections
 (/ for the last one,<=0 for list) >
```

You will need to select this ψ-scan in order to apply the non-spherical component to the absorption. Enter '**/**' or '**1**' to select it.

```
Reflection  14  8  0 was measured    37 times
 These measurements, given as IREF, PSI, and Intensity, are
1461   0.00    246. 1462  10.00    234. 1463  20.00    199. 1464  30.00    234.
1465  40.00    235. 1466  50.00    223. 1467  60.00    235. 1468  70.00    249.
1469  80.00    243. 1470  90.00    260. 1471 100.00    272. 1472 110.00    261.
1473 120.00    257. 1474 130.00    291. 1475 140.00    292. 1476 150.00    290.
1477 160.00    279. 1478 170.00    266. 1479-180.00    224. 1480-170.00    243.
1481-160.00    202. 1482-150.00    218. 1483-140.00    219. 1484-130.00    205.
1485-120.00    219. 1486-110.00    233. 1487-100.00    247. 1488 -90.00    207.
1489 -80.00    233. 1490 -70.00    248. 1491 -60.00    279. 1492 -50.00    281.
1493 -40.00    318. 1494 -30.00    282. 1495 -20.00    278. 1496 -10.00    279.
1497   0.00    265.
Do you wish to copy them to the .EXP file? (<Y>,N) >
```

This listing shows the measured intensity for all occurrences of the selected ψ-scan reflection in the data set. You should examine it with some care because one that is out of sequence with the others is not part of the ψ-scan and belongs in the reflection data set. You will want to copy the ψ-scan data to the EXP file, so enter **'Y'**.

```
Copy all of this set? (<?>,Y,N) >
```

This question gives you the opportunity to exclude some of the reflections from the ψ-scan set. For example, those observations that were collected during the normal data collection and not part of a ψ-scan could be skipped. In the present case, however, you will want to copy all of them to the EXP file, so enter **'Y'**.

```
Are you finished with the PSI scan data? (<Y>,N) >
```

We are finished with the ψ-scan data, so enter **'Y'**. The display will change the number of reflections until the entire data set is processed after which the **CAD4RD** program will terminate.

```
1475 reflections have been processed
<sigma(I)>/<I> =  0.017
CAD4RD run ended successfully
  The experiment is OXONIUM  creation date = 20-JUN-1994 10:51:07.67
MIST::GSAS Command? >
```

While you were running **CAD4RD**, it was also producing much of the output seen on the screen on the list file. You can examine it by using either of the **GSAS** utilities **ELST** or **TLST**.

Absorption Correction Setup and Calculations

You will need to run **EXPEDT** to set up the absorption calculations. This includes selecting the method for calculating the absorption and entering some coefficients. Enter **'EXPEDT'** at the **GSAS** prompt to get started.

```
                 |------------------------------------------|
                 |       Program EXPEDT Version 6.50        |
                 | A menu driven routine to edit .EXP files |
                 | Distributed on TEST Vers. 20-JUN-1994    |
                 |------------------------------------------|
       |----------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele           |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
       |                                                               |
       | Copyright, 1994, The Regents of the University of California. |
       |----------------------------------------------------------------|

The last history record is :
    HSTRY  1 CAD4RD  V-6.14   20-JUN-94 10:51:17
Is this the file you wish to use? (<?>,D,K,N,Q,R,Y) >
```

To make a copy of this experiment file and commence editing enter **'Y'**. If you are brave you can use the **'K'** option which skips the copy operation. Be aware that if you mess up the edit you will have to live with it because the **'Q'**uit option is not available when the **'K'**eep option is selected.

```
Experiment title:
         Single Crystal Exercise
The last history record is :
    HSTRY  1 CAD4RD  V-6.14   20-JUN-94 10:51:17
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

The absorption correction setup is one of the controls for single crystal data preparation, so enter **'S'**.

```
Enter Single Crystal data preparation option(<?>,A,D,I,L,P,T,U,X) >
```

You should look at this menu further, so enter **'CR'** to get the help listing.

```
The available options are:
<?> - Type this help listing
A       - Enter and edit data for SCABS
D n/n:m - Do not use histograms
I       - Enter or change instrument parameter file
L       - List histogram titles
P       - Edit phase information
T       - Change the experiment title
U n/n:m - Use histograms
X       - Exit from single crystal data editing
Enter Single Crystal data preparation option(<?>,A,D,I,L,P,T,U,X) >
```

You need to set up the controls for single crystal absorption calculations by **SCABS** so enter **'A'**.

```
The absorption flag is                    NONE
The radiation type flag is                MoKa
The absorption coefficient is       0.000
The maximum value of d* to be used is  2.000
The instrument error constant is      0.0100
PSI scan data is present
 Scan   1 was measured with the 14  8  0 reflection
 There are  37 values
 PSI  Value    PSI  Value    PSI  Value    PSI  Value    PSI  Value
   0.0 0.9841   10.0 0.9372   20.0 0.7982   30.0 0.9360   40.0 0.9400
  50.0 0.8914   60.0 0.9389   70.0 0.9972   80.0 0.9715   90.0 1.0401
 100.0 1.0904  110.0 1.0429  120.0 1.0281  130.0 1.1630  140.0 1.1687
 150.0 1.1607  160.0 1.1167  170.0 1.0664 -180.0 0.8971 -170.0 0.9743
-160.0 0.8085 -150.0 0.8720 -140.0 0.8748 -130.0 0.8194 -120.0 0.8766
-110.0 0.9314 -100.0 0.9875  -90.0 0.8268  -80.0 0.9343  -70.0 0.9921
 -60.0 1.1167  -50.0 1.1236  -40.0 1.2734  -30.0 1.1293  -20.0 1.1127
 -10.0 1.1179    0.0 1.0601

 Reflection data will not be listed in SCABS
The Absorption type is currently NONE
Enter absorption type desired (<?>,A,G,N,P,S,W,X) >
```

A summary of the available data for the absorption correction including theψ-scan data is listed. Another new menu, let us look at it by typing **'?'**.

```
The absorption types available are
 <?> - Repeat this help message
 A  - Crystal described by 25 or fewer planes
          Absorption calculated analytically
 G  - Crystal described by 25 or fewer planes
          Absorption by Gauss approximation
 N  - No absorption is to be applied
 P  - PSI-scan data will be used
 S  - Assume a spherical crystal
 W  - Spherical crystal, modified by PSI-scan data
 X  - Exit from absorption type editing
The Absorption type is currently NONE
Enter absorption type desired (<?>,A,G,N,P,S,W,X) >
```

The type of correction that you will use on this data is a combination of a sphere andψ-scan data. Enter **'W'** to accomplish this.

```
Radius of the sphere in mm.? >
```

The crystal was approximately a 0.2 mm cube, you can assume a .3mm sphere as a good approximation, so enter **'0.15'** to define the radius of the sphere.

```
Do you wish to modify the PSI scan data? (Y,<N>) >
```

No, don't modify the ψ scan data, so enter either **'N'** or **'CR'**.

```
The Absorption type is currently SPHR+PSI
Enter absorption type desired (<?>,A,G,N,P,S,W,X) >
```

You have completed the absorption correction setup so enter **'X'** to exit.

```
SCABS control data editing option (<?>,A,D,F,I,L,M,P,R,X) >
```

Enter **'X'** to exit from **SCABS** control editing.

```
Enter Single Crystal data preparation option(<?>,A,D,I,L,P,T,U,X) >
```

Enter **'X'** to exit from single crystal data editing.

```
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

You are finished with **EXPEDT** for now, so enter **'X'** to exit from **EXPEDT**.

```
EXPEDT terminated successfully
  The experiment is OXONIUM  creation date = 20-JUN-1994 10:51:07.67
MIST::GSAS Command? >
```

Now you are ready to perform the absorption calculations. Enter **'SCABS'** to perform the absorption calculations. This may be run as a batch job on VMS systems or in background on UNIX systems. This job will complete in a few minutes and the output is sent to the list file. Some output will appear on the screen if it is run "online" (or in foreground). When it finishes you are ready for the next step.

Intensity Statistics

After the **SCABS** run completes, you can run **ISTATS** to check on the proper choice of space group. This data set was collected for the primitive space group Pm–3 and it is of interest to check the intensity of the various parity classes to determine the correct space group. Enter **'ISTATS'** at the **GSAS** prompt. The following output will appear on both the screen and the list file. The reflection classes that should be extinct for Ib3 are marked in the manual by asterisks (not in the screen output though), you should look for them on your screen.

```
               |-----------------------------------------------|
               |         Program ISTATS Version 6.14           |
               | Program for determining reflection statistics |
               |    Distributed on TEST Vers. 20-JUN-1994      |
               |-----------------------------------------------|
       |---------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele           |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
       |                                                               |
       | Copyright, 1994, The Regents of the University of California. |
       |---------------------------------------------------------------|

There are  1 histograms
Histogram will be used in least-squares
Histogram 1 has 1460 reflections

Refln1460

Set     Parity      n  <F/sF>   n>3s  n>9s  Max(F/sF)
h00     h = 2n      3  78.024     3     3     83.31
h00     h = 2n+1    2   0.284     0     0      1.48       *
0k0     k = 2n      8  59.157     8     8     83.05
0k0     k = 2n+1    7  -0.456     0     0      0.63       *
00l     l = 2n      8  58.015     8     8     81.39
00l     l = 2n+1    7  -0.778     0     0      0.93       *
hk0     h = 2n     57  33.732    30    30     91.50
hk0     h = 2n+1   49   0.626     3     1     10.10       **
hk0     k = 2n     55  35.290    30    30     91.50
hk0     k = 2n+1   51   0.245     3     1     10.10       **
hk0   h+k = 2n     54  36.190    33    31     91.50
hk0   h+k = 2n+1   52  -0.016     0     0      2.56       *
h0l     h = 2n     64  31.280    33    33     90.11
h0l     h = 2n+1   49   0.370     1     0      8.65       **
h0l     l = 2n     58  34.639    33    33     90.11
h0l     l = 2n+1   55   0.200     1     0      8.65       **
h0l   h+l = 2n     57  35.647    34    33     90.11
h0l   h+l = 2n+1   56  -0.211     0     0      1.88       *
0kl     k = 2n    117  27.626    61    61     91.91
0kl     k = 2n+1  108   1.747    21     6     24.00       **
0kl     l = 2n    117  27.665    61    61     91.91
0kl     l = 2n+1  108   1.705    21     6     24.00       **
0kl   k+l = 2n    113  30.467    82    67     91.91
0kl   k+l = 2n+1  112  -0.194     0     0      1.80       *
hkl   h+k = 2n    733  17.245   272   251     91.91
hkl   h+k = 2n+1  727   3.347   163    79     65.51
hkl   h+l = 2n    734  17.256   276   246     91.91
hkl   h+l = 2n+1  726   3.316   159    84     65.51
hkl   k+l = 2n    733  18.027   323   269     91.91
hkl   k+l = 2n+1  727   2.559   112    61     64.52
hkl h+k+l = 2n    734  20.612   435   330     91.91
hkl h+k+l = 2n+1  726  -0.076     0     0      2.70       *
hhl     l = 2n     58  38.428    49    44     91.50
hhl     l = 2n+1   53   0.005     0     0      2.70       *
hhl   h+l = 2n     56  34.648    33    33     91.50
hhl   h+l = 2n+1   55   5.250    16    11     64.29
hhh     h = 2n      3  77.659     3     3     91.50
hhh     h = 2n+1    3   0.680     0     0      2.64       *
  The experiment is OXONIUM  creation date = 20-JUN-1994 10:51:07.67
MIST::GSAS Command? >expedt
```

As you can see we collected a data set for the primitive lattice. There is no doubt about the I-lattice centering, however the evidence that the space group should really be $I2_13$ is very weak. The extra extinctions needed for Ib3 (marked **) do not show much more intensity than the extinctions common to both space groups (marked *). For the remainder of this exercise we have assumed that Ib3 is the correct choice.

Data Merge and Patterson Calculations

The next step is to merge the equivalent reflections to give the unique set for the space group Ib3. However, you can save a little time by setting up a Patterson calculation and running the data merge program and the Fourier calculations in sequence. Thus, the first step here is to enter **'EXPEDT'** for the Fourier setup of a Patterson map.

```
                 |-------------------------------------------|
                 |       Program EXPEDT Version 6.50         |
                 | A menu driven routine to edit .EXP files  |
                 | Distributed on TEST Vers. 20-JUN-1994     |
                 |-------------------------------------------|
       |----------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele            |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805      |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545     |
       |                                                                |
       | Copyright, 1994, The Regents of the University of California. |
       |----------------------------------------------------------------|

The last history record is :
    HSTRY  3 SCABS   V-6.16   20-JUN-94 10:57:21 Finished
Is this the file you wish to use? (<?>,D,K,N,Q,R,Y) >
```

To start editing Fourier controls enter **'K F'**. The current experiment file will be opened for editing.

```
Experiment title:
         Single Crystal Exercise
The last history record is :
    HSTRY  3 SCABS   V-6.16   20-JUN-94 10:57:21 Finished
Enter desired map (<?>,DELF,FCLC,FOBS,PTSN,DPTS,EXIT) >
```

You want to calculate a Patterson map, enter **'PTSN'**. **GSAS** will properly compute the Patterson map so that the symmetry is appropriate for the space group Ib3.

```
Enter section desired (X,Y,Z) >
```

Since the unit cell is cubic the choice is immaterial, enter **'X'**.

```
Do you wish to specify individual map steps for each axis (Y/<N>)? >
```

It is not necessary to make the map steps different for the three axes, enter **'CR'**.

```
Current overall map step size is  0.2000 A
Enter new overall map step size in Angstroms >
```

You can get a little better definition of the peak locations with a finer step size than the default, enter **'0.1'**.

```
The a-axis is  10.120001 A
The new del-x is  0.1012 A
The cell will be divided into  100 points along x
The b-axis is  10.120001 A
The new del-y is  0.1012 A
The cell will be divided into  100 points along y
The c-axis is  10.120001 A
The new del-z is  0.1012 A
The cell will be divided into  100 points along z
Old x limits are  0.0000 to  0.0000
Enter minimum and maximum values of x in fractions of the cell edge >
```

The output shows the number of steps it finds along each cell edge. The next step is to determine the fraction of the cell edge that is the minimum needed to generate a complete map. Reference to the 'International Tables for X-ray Crystallography Vol. A' for this space group suggest that you should enter the limits **'0 1/4 0 1/4 0 1/2'**.

```
New x limits are  0.0000 to  0.2500
Old y limits are  0.0000 to  0.0000
New y limits are  0.0000 to  0.2500
Old z limits are  0.0000 to  0.0000
New z limits are  0.0000 to  0.5000
At least one asymmetric part of the unit cell is included in the Fourier.
Enter new list of histogram numbers in the order you wish them to be read.
The last occurrence of a reflection will be used.
Include histogram (0 to terminate list) >
```

You entered a sufficient part of the cell to be calculated so that all the unique part of the map is covered. Next you need to select the histograms that are the source of the structure factors needed for the calculation of the Patterson. There is only one histogram available so enter **'1 0'** to include it and terminate the list.

```
Enter FOURIER map calculation option (<?>,A,D,E,F,H,I,L,M,P,R,S,T,W,X) >
```

You are all done entering the Fourier controls so enter **'X'**.

```
At least one asymmetric part of the unit cell is included in the Fourier.
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

You are reassured that the choice of limits is at least one asymmetric unit and you are all finished in **EXPEDT** so enter **'X'** to exit.

```
EXPEDT terminated successfully
  The experiment is OXONIUM  creation date = 20-JUN-1994 10:51:07.67
MIST::GSAS Command? >scmerge fourier
```

Now you are ready for the data merge that we put off from above and the Patterson map calculation. On VMS systems enter **'SCMERGE FOURIER'** and respond to the two sets of batch job questions about log files and queues. On UNIX systems run them sequentially in either foreground or background. The **SCMERGE** program will take longer to run than any of the previous batch jobs in this exercise; however **FOURIER** is quite fast. Both programs will produce results on the list file, consult them at your leisure. After they both finish you will be ready for the map search step.

Map Search and Structure Solution

After the two jobs you submitted above have completed, you will need to determine the location of peaks in the Patterson map. The program **FORSRH** will do this for you, so at the **GSAS** prompt enter **'FORSRH'** and you will get the following screen.

```
                  |-----------------------------------------|
                  |      Program FORSRH Version 6.16        |
                  |     Fourier map peak search program     |
                  | Distributed on TEST Vers. 20-JUN-1994   |
                  |-----------------------------------------|
       |---------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele           |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
       |                                                               |
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       |---------------------------------------------------------------|

A PTSN file has been opened
The range of map values is -239.091 to 9373.339
Enter min. Peak value (negative if negative values are desired) >
```

The program **FORSRH** opens the PTSN map file and lists the extreme limits on the map density. You are being asked to set the minimum peak value cutoff for the search. For this search you should enter **'50'** to locate all peaks greater than 50. If you were interested in negative peaks as well as positive peaks you could enter a negative number.

```
Enter number of peaks to be located (1 to 225) >
```

The program wants a maximum number of peaks to save, before raising the cutoff value. Enter **'50'** as a reasonable maximum. Thus, the number of peaks listed will be limited to 50 and all will have a density greater than 50.

```
Save the peaks located in the EXP file? (Y,<N>) >
```

There is no need to save these peak locations in the experiment file, so enter **'N'** and wait for the program to scan the Patterson map and then list out its findings.

```
Min rho =   50.00000  No. of peaks =  50  Peaks saved?

The following vectors were found
           Rho       X       Y       Z         Length
   1    9373.339  0.0000  0.0000  0.0000        0.00
   2    8617.319  0.0000  0.0000  0.5000        5.06
   3    1236.617  0.2500  0.2500  0.2500        4.38
   4     329.964  0.1373  0.1019  0.4403        4.78
   5     300.689  0.1023  0.0610  0.3649        3.88
   6     299.863  0.0615  0.1351  0.1034        1.83
   7     293.569  0.0617  0.1353  0.3968        4.29

Total CPU time for FORSRH was   0.49 seconds
FORSRH terminated successfully.
  The experiment is OXONIUM  creation date = 20-JUN-1994 10:51:07.67
MIST::GSAS Command? >
```

After a brief summary of the limits imposed on the peaks list, **FORSRH** finds that the Patterson map has only seven unique peaks. It noted that it was dealing with a Patterson vector map and modified the space group operations properly to determine the unique set of peaks in the map. You might want to examine the Patterson map with either **PLOTTER** or **FORPLOT**, or both at this point.

We know that there are only eight antimony atoms in the unit cell, so we can assume that they are in set 8a at 0,0,0 and the eight oxygen atoms are in set 8b at 1/4,1/4,1/4. Your only task in solving this structure is to choose the Sb-F vector from the remaining four peaks. The choice of space group as Ib3 makes this task easier in that one of the four xyz values is the location of the fluorine atom. Remembering that the lattice parameter is ~10Å, peak number 6 is about the right length (1.83Å) for a Sb-F bond. However, the vector shown points in the direction of the oxygen atom at 1/4,1/4,1/4 so you must choose an alternate location for the fluorine atom. A good choice is to change one sign so the fluorine atom would be at -x,y,z or -0.0615,0.1351,0.1034.

Atom Insertion and Structure Refinement

After you have solved the Patterson, you will need to run **EXPEDT** to enter the atoms into the experiment file and set some least squares controls. Since you have done these operations for both powder exercises we want to demonstrate to the power of the type ahead features in **GSAS** by entering as much as possible long strings of commands. Be very careful when you type them in so that the correct sequence will be executed. To start enter **'EXPEDT'** at the **GSAS** prompt, the following familiar screen will appear.

```
                  |------------------------------------------|
                  |       Program EXPEDT Version 6.50        |
                  | A menu driven routine to edit .EXP files |
                  | Distributed on TEST Vers. 20-JUN-1994    |
                  |------------------------------------------|
        |---------------------------------------------------------------|
        |            Allen C. Larson and Robert B. Von Dreele           |
        |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
        |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
        |                                                               |
        | Copyright, 1994, The Regents of the University of California. |
        |---------------------------------------------------------------|

The last history record is :
    HSTRY  5 SCMERGE V-6.14   20-JUN-94 10:58:54
Is this the file you wish to use? (<?>,D,K,N,Q,R,Y) >
```

The first steps are to open this experiment file, enter least-squares editing and then atom editing. Enter **'K L A'** to get there.

```
Experiment title:
         Single Crystal Exercise
The last history record is :
    HSTRY  5 SCMERGE V-6.14   20-JUN-94 10:58:54

Phase No. 1 There are   0 atoms for this phase
Title: (H3O)+(SbF6)-
Give atom editing command (<?>,$,I,S,X) >
```

Some of the information lines appear before you see the atom editing line. Notice that there are no atoms, you will now enter the three for (H$_3$O)$^+$(SbF$_6$)$^-$. Start by entering **'I 1'**.

```
Enter TYPE, X, Y, Z, FRAC or <?> for help
  >
```

Now enter the antimony atom. It is at the origin and we will take defaults for the name and temperature factor. Enter **'SB 0 0 0 1 / I** /'. Don't worry if the input line wraps on your terminal, all the characters will be accepted. Next you see the data you entered for the antimony atom.

```
SER TYPE    X       Y       Z      FRAC    NAME    UISO    CODE  STSYM  MULT FXU
  1 SB   0.00000 0.00000 0.00000 1.00000 SB(1)     0.02500 I     -3(111)   8 000

Phase No. 1 There are   1 atoms for this phase
Title: (H3O)+(SbF6)-
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

Next you need to enter the oxygen atom coordinates; for the other data you will use defaults. Enter **'I N O 1/4 1/4 1/4 1 / I** /', again don't worry about the line wrap.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM  MULT FXU
  2 O    0.25000 0.25000 0.25000 1.00000 O(2)     0.02500 I     -3(111)   8 000

Phase No. 1 There are   2 atoms for this phase
Title: (H3O)+(SbF6)-
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

Finally, enter the fluorine atom parameters. Enter **'I N F -0.0615 0.1351 0.1034 1 / I /'**. As you can see quite long strings of commands can be entered into **GSAS**; you will probably never exceed the 132 character buffer available for user input.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM  MULT FXU
  3 F   -0.06150 0.13510 0.10340 1.00000 F(3)     0.02500 I        1     48 000

Phase No. 1 There are   3 atoms for this phase
Title: (H3O)+(SbF6)-
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

The next step is to set the flags for refinement of the atom coordinates and temperature factors. Enter **'V 1:3 X U'**. This sets the flags for all three atoms.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM  MULT FXU
  1 SB   0.00000 0.00000 0.00000 1.00000 SB(1)    0.02500 I XU  -3(111)   8 000
  2 O    0.25000 0.25000 0.25000 1.00000 O(2)     0.02500 I XU  -3(111)   8 000
  3 F   -0.06150 0.13510 0.10340 1.00000 F(3)     0.02500 I XU     1     48 000

Phase No. 1 There are   3 atoms for this phase
Title: (H3O)+(SbF6)-
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

Notice that the flags to refine coordinates for the Sb and O atoms were both set by this command. **GSAS** will use the symmetry information to hold these values fixed regardless of the refinement flag because both atoms are in special positions. You are finished with atom editing, enter **'X'**

```
Select editing option for Least Squares calculation (<?>,A,B,F,L,O,R,S,T,X) >
```

The next step is to modify the least-squares controls, enter **'L'** to see the menu.

```
Maximum number of cycles is   3
Refine on Fsq
The Single crystal Least Squares weight function is
  W = Wght
 Wght = 1.0/(SigmaFoSq)**2 for FoSq refinements
 Wght = (2*Fo/SigmaFoSq)**2 for Fo refinements
Minimum D-spacing is  0.000
Maximum D-spacing is 99.990
Include all data as observed
Enter L-S control editing option (<?>,C,F,G,I,K,L,M,N,P,S,W,X) >
```

You are told the defaults for single crystal refinements. Enter **'CR'** to see the help listing.

```
 C n - maximum number of cycles
 F   - Change minimization function
 G a - Upper limit on wave-length for SCD data
 I a - Treatment of Negative Obs.
 L   - List current settings
 M n - upper D-spacing limit
 N n - lower D-spacing limit
 P   - Select options for the output listing
 R   - Change the weight modification flag, Robust
 S n - Set a Lower I/SigI cut-off in RFN-F
 U n - Set a Upper I/SigI cut-off in RFN-F
 W n - refinement weight option "n"
 X   - Exit from editing least squares controls
Enter L-S control editing option (<?>,C,F,G,I,K,L,M,N,P,S,W,X) >
```

The modifications that we want you to do are to change the number of least squares cycles to 5, set the I/σI cutoff to 1.5, and set the refinement to be on F rather than F^2. To do all of these enter **'C 5 S 1.5 F N X'**. Some messages will appear as each value is set and you will exit from this menu.

```
Maximum number of cycles is   5
Lower I/SigI cut-off for F refinements is  1.500
Refine on F
Select editing option for Least Squares calculation (<?>,A,B,F,L,O,R,S,T,X) >
```

The last step is to modify the scale factor so that the starting value is closer to what you will obtain when the least squares converges. Normally you would have refined this value first before moving the atoms, but you will change it here this way for the purposes of this exercise. To change this overall parameter enter **'O H C 0.4 X X X'**. Some messages will appear as the scale is changed. You need not set the refinement flag, it is set 'Y' by default.

```
Editing histogram scale factors
Histogram will be used in least-squares

Histo. scale =      1.0000     Refine Y Damping flag =  0
Histogram will be used in least-squares

Histo. scale =     0.40000     Refine Y Damping flag =  0
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

The sequence of exit commands in your last command string brought you to the last menu in **EXPEDT**. This menu can only be exited (and hence out of **EXPEDT**) by entering an **'X'** on a new line. Do that now.

```
EXPEDT terminated successfully
  The experiment is OXONIUM  creation date = 20-JUN-1994 10:51:07.67
MIST::GSAS Command? >
```

The atoms are entered and the least squares controls are now set. Enter **'GENLES'** at the **GSAS** prompt and respond to the log file and queue questions. The run will take a few minutes; when it finishes you can examine the results in the list file.

Anisotropic Refinement and Structure Results

After **GENLES** finishes and you have satisfied yourself that all is going well if might be useful to convert the thermal parameters to anisotropic and then make another pass through **GENLES** followed by a distance and angle calculation and an analysis of the thermal ellipsoids with **DISAGL** and **BIJCALC**. As for the previous section, you will enter several commands in sequence so that the changes are made with minimal output on the terminal. To begin enter **'EXPEDT'** at the **GSAS** prompt.

```
                 |------------------------------------------|
                 |       Program EXPEDT Version 6.50        |
                 | A menu driven routine to edit .EXP files |
                 | Distributed on TEST Vers. 20-JUN-1994    |
                 |------------------------------------------|
       |---------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele           |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
       |                                                               |
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       |---------------------------------------------------------------|

The last history record is :
    HSTRY  7 GENLES  V-6.48   20-JUN-94 11:02:12 Sdsq= 0.112E+05 S/E= 0.125E-03
Is this the file you wish to use? (<?>,D,K,N,Q,R,Y) >
```

First you need to select this version of the experiment file, least squares editing, atom editing and finally list the atoms. Enter **'K L A L'** to do all of these.

```
Experiment title:
         Single Crystal Exercise
The last history record is :
    HSTRY  7 GENLES  V-6.48   20-JUN-94 11:02:12 Sdsq= 0.112E+05 S/E= 0.125E-03

Phase No. 1 There are   3 atoms for this phase
Title: (H3O)+(SbF6)-
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM  MULT FXU
  1 SB   0.00000 0.00000 0.00000 1.00000 SB(1)    0.01511 I XU  -3(111)   8 000
  2 O    0.25000 0.25000 0.25000 1.00000 O(2)     0.03686 I XU  -3(111)   8 000
  3 F   -0.05996 0.14043 0.10432 1.00000 F(3)     0.02604 I XU     1     48 000

Phase No. 1 There are   3 atoms for this phase
Title: (H3O)+(SbF6)-
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

Now you want to make all the atoms anisotropic and then exit as far as possible, enter **'U 1:3 A X X X'**.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM  MULT FXU
  1 SB   0.00000 0.00000 0.00000 1.00000 SB(1)            A XU  -3(111)   8 000
U11,U22,U33,U12,U13,U23 =   0.01511  0.01511  0.01511  0.00000  0.00000  0.00000
  2 O    0.25000 0.25000 0.25000 1.00000 O(2)             A XU  -3(111)   8 000
U11,U22,U33,U12,U13,U23 =   0.03686  0.03686  0.03686  0.00000  0.00000  0.00000
  3 F   -0.05996 0.14043 0.10432 1.00000 F(3)             A XU     1     48 000
U11,U22,U33,U12,U13,U23 =   0.02604  0.02604  0.02604  0.00000  0.00000  0.00000

Phase No. 1 There are   3 atoms for this phase
Title: (H3O)+(SbF6)-
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

The equivalent anisotropic thermal parameters for each of the atoms is listed and then the last menu in **EXPEDT** is shown. To exit from this one you must enter **'X'** on a new line, do this now.

```
EXPEDT terminated successfully
  The experiment is OXONIUM  creation date = 20-JUN-1994 11:02:07.65
MIST::GSAS Command? >
```

To finish the refinement and calculate some structural results enter **'GENLES DISAGL BIJCALC'** (for VMS systems) and respond to the three pairs of batch questions. The results of these calculations can be found in your list file. You can next work on refining the structure in the correct space group ($I2_13$) as indicated by the relatively few observed *hk0* reflections with *h* and *k* odd seen in the **ISTATS** run.

Structure Drawing

The last part of this exercise consists of an introduction to the structure drawing program **ORTEP**. **ORTEP** was originally written many years ago by C. Johnson of Oak Ridge National Laboratory and it has become one of the most widely used programs for drawing crystal structures. We have modified it for use in **GSAS** to make an interactive version using the **GSAS** menu handling facilities. Most of the original features of **ORTEP** have been retained in this version. We have assumed that you have refined the structure of $(H_3O)^+$ $(SbF_6)^-$ in the space group Ib3 with anisotropic thermal parameters. To begin enter **'ORTEP'** at the **GSAS** prompt.

```
            |----------------------------------------------------|
            |            Program ORTEP Version 6.17              |
            | Crystal structure plotting program by C.K. Johnson |
            |      Distributed on TEST Vers. 20-JUN-1994         |
            |----------------------------------------------------|
       |---------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele           |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805     |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545    |
       |                                                               |
       | Copyright, 1994, The Regents of the University of California. |
       |---------------------------------------------------------------|

Enter terminal type (<?>,A,B,C,D,E,F,G,H,Z) >
```

As usual for this question enter your terminal type and an **'N'** to avoid creation of a hard copy file. **ORTEP** will next read information from your experiment file and produce a summary of what it found. If you are working in one of the four face-centered cubic space groups that have 192 symmetry operators (Fm3m, etc.), **ORTEP** will reduce the symmetry and add extra atoms as necessary to give 96 operators.

```
Title: Single Crystal Exercise
Phase name: (H3O)+(SbF6)-
Lattice parameters:
a,b,c            =    10.1200   10.1200   10.1200
alpha,beta,gamma =     90.000    90.000    90.000

Space group   I b 3
The lattice is centric  I-centered cubic         Laue symmetry m 3
 Multiplicity of a general site is  48
 The symmetry of the point 0,0,0 contains 1bar

The equivalent positions are:

 ( 1)     X      Y      Z   ( 2)     Z      X      Y   ( 3)     Y      Z      X
 ( 4)     X  1/2+Y  1/2-Z   ( 5) 1/2-Z      X  1/2+Y   ( 6) 1/2+Y  1/2-Z      X
 ( 7) 1/2-Z  1/2+X     -Y   ( 8)    -Y  1/2-Z  1/2+X   ( 9) 1/2+Y     -Z  1/2-X
 (10) 1/2-X  1/2+Y     -Z   (11)    -Z  1/2-X  1/2+Y   (12) 1/2+X     -Y  1/2-Z

Do you want atom list (Y/<N>)? >
```

If you respond **'Y'** here the atoms will be listed, to skip that enter **'N'**. After the atoms are read in the list is examined for duplicate coordinates and the extra atoms are removed from the list. Two additional atoms are added, one is at the unit cell origin and the other is at the unit cell center.

```
New crystal to cartesian transformation matrix:
   0.09881   0.00000   0.00000
   0.00000   0.09881   0.00000
   0.00000   0.00000   0.09881
No atoms in drawing array
Atom names:
  1 SB(1)      2 O(2)      3 F(3)      4 ORIGIN     5 CENTER
Enter model building command (<?>,A,B,D,E,L,S,T,U,X) >
```

The first step is to select a set of atoms to be drawn by **ORTEP**. Most of the facilities in the original version are available as menu selections. You presently have no atoms selected for drawing. Enter **'CR'** to see the help listing.

```
Model building commands:
 <?> - Type this help listing
 A   - Atom designator codes (ADC)
 B   - Box of enclosure
 D   - Subsequent commands will DELETE atoms
 E   - Erase all atoms
 L   - List current contents of atom array
 S   - Sphere of enclosure
 T   - Triclinic cell of enclosure
 U   - Insert unit cell corners
 X   - Exit model building
ADC is the code "acccss" where a is the atom sequence number, ccc is unit cell
designators (1-9) and ss is the symmetry operator number. If a positive ADC is
followed by a negative ADC then all atoms between them are included. Ex. 155501
for 1st atom in center cell & 1st operator; 155501 -2455504 for all atoms in
center cell between atoms 1 and 24 for operators 1 to 4.
Enter <CR> to continue
```

These commands allow you to select single atoms, sets of atoms, all atoms within certain volumes and can even cause chains of atoms to be selected. The atoms are designated by **ORTEP** by a "atom designator code" (ADC) which has three parts. The first part is the atom serial number as listed by **ORTEP**. See the atom name list above for these values. The second part is a three integer code that indicates which unit cell the atom is in. **ORTEP** will permit unit cell designation within a 9x9x9 block of unit cells. The designation "555" refers to the central unit cell within this block. The last part of the ADC is a two integer designator for the symmetry operator. Thus an ADC looks like "acccss" as noted in the help listing. For example, the code "355602" refers to atom number 3, located in unit cell 556 generated from the original position by symmetry operator number 2. Enter **'CR'** to continue.

```
Atom names:
  1 SB(1)      2 O(2)      3 F(3)      4 ORIGIN     5 CENTER
Enter model building command (<?>,A,B,D,E,L,S,T,U,X) >
```

We want you to draw the SbF_6^- ion; to begin you need to select the Sb atom. Enter **'A'** for individual atom selection.

```
Enter  atom designator code (0 to quit,-1 for help) >
```

You want to include the Sb atom in the center cell and first symmetry operator, enter **'155501'**

```
Enter  atom designator code (0 to quit,-1 for help) >
```

That is the only atom you want to select that way, enter **'0'** to terminate individual atom selection.

```
Atom names:
  1 SB(1)      2 O(2)       3 F(3)       4 ORIGIN     5 CENTER
Enter model building command (<?>,A,B,C,D,E,L,R,S,T,U,X) >
```

The easiest way to select the six F atoms is to include those that are inside a sphere about the Sb atom, enter **'S'** to use this option.

```
Enter first origin atom designator code (0 to quit,-1 for help) >
```

The sphere of inclusion can be constructed about a range of atoms. In this case you only want a sphere around just the Sb atom, enter the ADC **'155501'** for it.

```
Enter last  origin atom designator code (0 to quit,-1 for help) >
```

In this case, the list of origin atoms in this case is terminated by the same atom, enter **'155501'**.

```
Enter first target atom number >
```

You want F atoms to be selected when they fall inside the sphere. Since F is the third atom in the list enter **'3'**.

```
Enter last target atom number >
```

Again a range of atoms can be selected if they fall inside the sphere of inclusion. In this case you only want F atoms so enter **'3'** again.

```
Enter max. interatomic bonding distance >
```

You only want those F atoms that are bonded to the Sb atom. The Sb-F bond length is somewhat less than 2Å, so enter **'2.0'**. **ORTEP** will find all atom number 3's that fall within 2Å of the already included Sb atom.

```
Atom names:
  1 SB(1)      2 O(2)       3 F(3)       4 ORIGIN     5 CENTER
Enter model building command (<?>,A,B,C,D,E,L,R,S,T,U,X) >
```

To list the atom ADC's that **ORTEP** found enter **'L'**.

```
Contents of drawing array:
   155501   355501   355502   355503   355513   355514   355515
Drawing array contains  7 atoms
Atom names:
  1 SB(1)      2 O(2)       3 F(3)       4 ORIGIN     5 CENTER
Enter model building command (<?>,A,B,C,D,E,L,R,S,T,U,X) >
```

As you had hoped there is seven atoms in the list, one Sb and six F atoms. Notice that although all seven atoms are in the same unit cell (555), the symmetry operators for the atoms selected might have been difficult to determine manually. You are finished here so enter **'X'**. As you exit from this menu **ORTEP** writes this atom selection list on the experiment file so that when you reenter **ORTEP** later they are read automatically.

```
Enter ORTEP command (<?>,B,C,E,L,M,N,P,R,S,T,U,V,Q) >
```

You are now in the main **ORTEP** menu. This menu was skipped earlier when **ORTEP** found that no atoms had been selected for drawing. Enter **'CR'** to see the help listing.

```
ORTEP commands:
 <?>   - Type this help listing
 B     - Edit bond selection controls
 C     - Select origin at centroid & give best view
 E e   - Choose ellipsoid style e
 L     - List structure data
 M     - Build or modify structure model
 N n   - Select a new phase n
 P     - Plot model
 R a r - Enter axis (x,y,or z) and angle for rotation of current drawing
 S a r - Enter axis (x or y) and angle for stereo rotation of current drawing
 T     - Select title & label options
 U u   - Enter viewpoint
 V u v - Enter reference vectors "u" & "v"; resets transformation matrix
 Q     - Quit ORTEP
Enter ORTEP command (<?>,B,C,E,L,M,N,P,R,S,T,U,V,Q) >
```

The commands listed here allow you to position the object for drawing by selection of reference vectors or rotation from the previous orientation. There are also commands that determine the ellipsoid style for the atoms and permit labeling of the atoms. You need, however, to complete the model by instructing **ORTEP** how you want the interatomic bonds to be drawn. Enter **'B'** for bond selection.

```
There are no bond selection controls
Atom names:
  1 SB(1)      2 O(2)       3 F(3)       4 ORIGIN     5 CENTER
Enter bond selection command (<?>,I,L,X) >
```

ORTEP informs you that no bond information is present , lists the atom names and gives a short menu. Enter **'CR'** to see the help listing.

```
Bond selection editing commands:
 <?> - Type this help listing
 I   - Insert bond selection control
 L   - List current bond selection controls
 X   - Exit bond selection
Enter bond selection command (<?>,I,L,X) >
```

You want to make a bond selection so enter **'I'** to start.

```
Enter first origin atom number >
```

ORTEP draws bonds from one set of atoms to another set of atoms when the interatomic distance falls within a range of distances. You first have to select the origin set of atoms for the bond drawing. Enter **'1'** so that the bonds are drawn from the Sb atom.

```
Enter last origin atom number >
```

You need to terminate the list of origin atoms, enter **'1'**.

```
Enter first target atom number >
```

Next you have to select the range of target atoms for the bond drawing. Enter **'3'** so that the bonds are drawn to the F atoms.

```
Enter last target atom number >
```

Again the target atom list must be terminated, enter **'3'**.

```
Enter bond type (<1>,2,3,4,5) >
```

ORTEP now wants an indication of how the bond is to be drawn. The bond is drawn with "bond type"*2 number of lines. Enter **'3'** so that six lines are used for each bond.

```
Enter min. (>0.0) and max. bond length & radius >
```

ORTEP now wants the range of distances to use for selecting the bonds to be drawn. It also wants the radius of the stick that is drawn to form the bond. All of these are in Angstroms. Enter **'1 2 0.02'** to draw bonds 0.04Å thick between 1.0 and 2.0 Å long. When you are used to the input of the bond selection controls all eight of these values can be entered on a single line (i.e. **'1 1 3 3 3 1 2 0.02'**).

```
Enter bond selection command (<?>,D,I,L,X) >
```

To see the bond drawing control you have entered, type **'L'**.

```
Bond selection controls:
No.  Ori. ANR  Tar. ANR  Type    D-min   D-max   Radius
    1    1    1    3    3    3  1.0000  2.0000  0.0200
Atom names:
  1 SB(1)      2 O(2)       3 F(3)       4 ORIGIN     5 CENTER
Enter bond selection command (<?>,D,I,L,X) >
```

This is the only bond control needed so enter **'X'** to leave this menu. **ORTEP** writes this information on the experiment file.

```
Enter ORTEP command (<?>,B,C,E,L,M,N,P,R,S,T,U,V,Q) >
```

The next step is to set the viewing direction for the SbF_6^- ion. The "best" view is one that looks through the thinnest "diameter" of the molecule. To get the best view enter the **'C'** command.

```
Do you want the best view of the model (<Y>/N)? >
```

Respond with a **'CR'**, a best view through the ion is selected for drawing. After this command is done then any of the other positioning commands (**'R'** or **'V'**) may be used to further refine the viewing direction.

```
Enter ORTEP command (<?>,B,C,E,L,M,N,P,R,S,T,U,V,Q) >
```

Next you want to select the ellipsoid style, enter **'E'**.

```
Enter ellipsoid style (<?>,A,B,C,D) and scale >
```

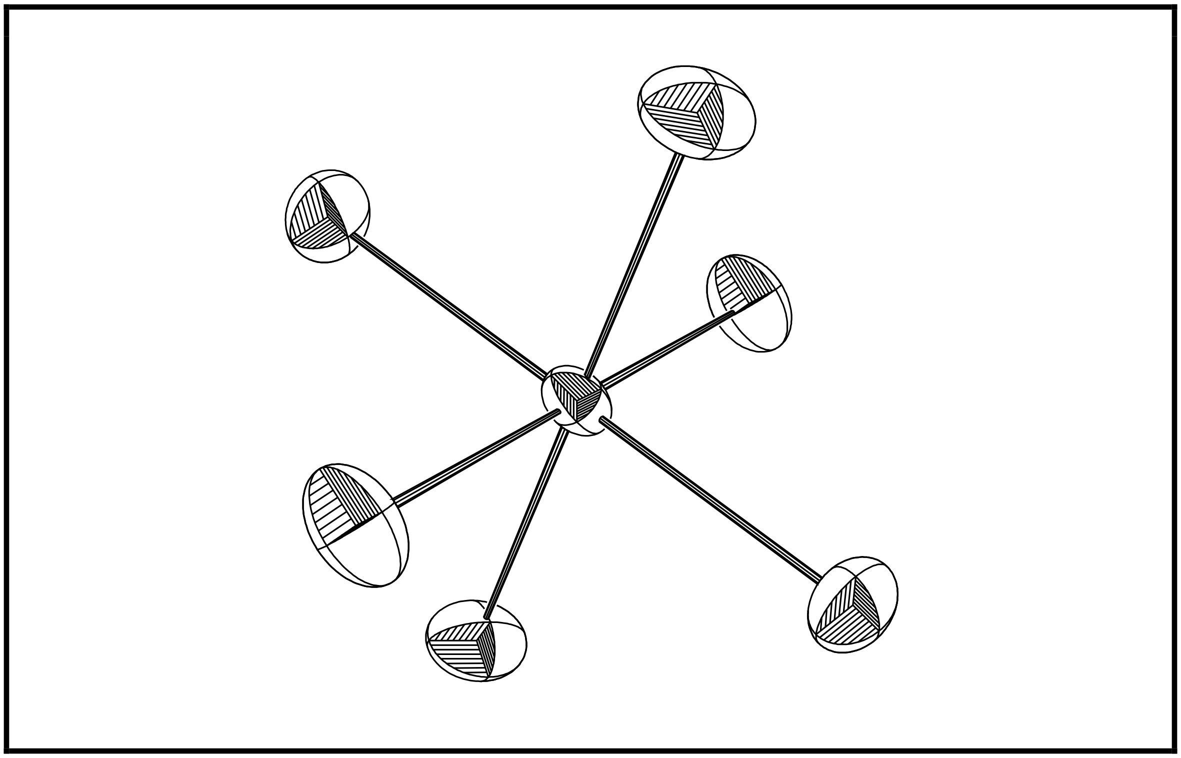
You may enter **'CR'** to see the help listing here, the **'A'** option displays the ellipsoids in the cross-hatched octant style so commonly seen in crystallographic publications.

```
Enter ellipsoid probability (default = 0.50) >
```

ORTEP now asks for the probability value that defines the ellipsoid surface to be plotted for each atom. To take the default enter '/'**.**

```
Enter ORTEP command (<?>,B,C,E,L,M,N,P,R,S,T,U,V,Q) >
```

The drawing is now ready to be plotted, enter **'P'** and the plot will immediately follow.



As usual enter **'CR'** to get the next prompt.

```
Enter ORTEP command (<?>,B,C,E,L,M,N,P,R,S,T,U,V,Q) >
```

You may wish to further explore the features of **ORTEP**. We recommend that you try different orientations, viewing positions and distances. Try the labeling options

(**'T'** command) especially the cursor controlled atom labeling feature. To exit from **ORTEP** enter **'Q'**.

```
ORTEP has finished
  The experiment is OXONIUM  creation date =  4-MAY-1994 16:28:08.62
MIST::GSAS Command? >
```

This completes the third exercise. Many of the **GSAS** programs used in this exercise wrote information to a list file. You should examine it with the **GSAS** utilities **ELST**, **TLST** and **SLST**.

Mathematical Basis

Introduction

In this section of the technical manual we describe the mathematical functions used in **GSAS** for the computation of various quantities and indicate the principal locations of the associated algorithms in the code. The routine names are in bold face.

Structure Factors

The structure factors, $F_{p,h}$, for both single crystal and powder data are computed in the standard way from atomic coordinates, atom form factors and temperature factors and the same expressions are used for both x-rays and neutrons. For the powder case, there is a set for each phase (p) in each histogram (h). The expression is the usual complex quantity

$$F_{p,h} = A_{p,h} + iB_{p,h}$$

where A and B are the cosine and sine parts of the structure factor (see below). If the structure is centrosymmetric and the inversion center is located at the unit cell origin then B is zero. Because of this simplifying process the space group routines in **GSAS** always place the inversion center at the origin. Since the observed intensity is related to the square of this quantity, the expression

$$F_c^2 = A^2 + B^2$$

is calculated for all diffraction data. Given that the atomic X-ray form factors also include anomalous dispersion contributions and are modified by atomic site fraction (x) and the thermal motion correction (T" - see below)

$$f = xT''(f_o + f' + if'')$$

the expressions for A and B are then broken down into three components each

$$A = A_o + A' - B''$$

$$B = B_o + B' + A''$$

where

$$A_o = \sum_i x_i T''_i f_{oi} \mathit{cos} 2\pi \mathbf{h \cdot r} \qquad B_o = \sum_i x_i T''_i f_{oi} \mathit{sin} 2\pi \mathbf{h \cdot r}$$

$$A' = \sum_i x_i T''_i f'_i \mathit{cos} 2\pi \mathbf{h \cdot r} \qquad B' = \sum_i x_i T''_i f'_i \mathit{sin} 2\pi \mathbf{h \cdot r}$$

$$A'' = \sum_i x_i T''_i f''_i \mathit{cos} 2\pi \mathbf{h \cdot r} \qquad B'' = \sum_i x_i T''_i f''_i \mathit{sin} 2\pi \mathbf{h \cdot r}$$

and the sums are over the unit cell contents. For neutrons the expressions are the same except that the form factors are generally just real scattering lengths (b_o). A few elements and isotopes show anomalous scattering so

$$f = xT''(b_o + ib')$$

In the powder case the averaging process means that the intensity for a single reflection includes contributions from Friedel reflection pairs. Thus the above components must be differently combined for the single crystal case to represent the powder intensity

$$F^2 = (A_o+A')^2 + B''^2 + (B_o+B')^2 + A''^2$$

In **GSAS** the atomic coordinates, site fractions and thermal motion parameters are refinable quantities. In addition, the anomalous dispersion contributions (f' and f'') for X-rays are also refinable.

The temperature factors are expressed as either U_{iso} or u_{ij} where the thermal correction to the structure factor is either

$$T'' = e^{-(8\pi^2 U_{iso} sin^2\Theta/\lambda^2)}$$

for isotropic thermal motion or

$$T'' = e^{-[2\pi^2(u_{11}h^2a^{*2} + \ldots + 2u_{12}hka^*b^* + \ldots)]}$$

for anisotropic thermal motion. Alternative forms for the temperature factors which may be more familiar are B_{iso} and β_{ij} where

$$B_{iso} = 8\pi^2 U_{iso}$$

and

$$\beta_{ij} = 2\pi^2 a_i^* a_j^* u_{ij}$$

The structure factors and their derivatives for x-rays and nuclear scattering of neutrons are calculated by subroutine **STRFCTR** for both powder and single crystal data.

Additionally, neutrons may also be scattered by ordered magnetic moments on some of the atoms in a crystal structure. In **GSAS** we assume that the neutron beam is unpolarized, i.e. the neutron spins are randomly oriented with respect to the diffraction vector. Thus, the total diffracted intensity is a simple sum of the nuclear and magnetic scattered intensities

$$F^2 = F^2_{nuc} + F^2_{mag}$$

The structure factor for magnetic scattering depends on both the magnitude of the magnetic cross section (p) and the magnetic interaction vector (**q**). Thus the structure factor is

$$\mathbf{F}_{mag} = \sum_i \mathbf{q}_i p_i e^{2\pi i \mathbf{h}\cdot\mathbf{x}_i}$$

which is a vector quantity and the sum is taken over all the magnetic atoms in the unit cell. Since there is no polarization, the magnetic scattered intensity is simply the square of the magnitude of $\mathbf{F}_{mag}$. The magnetic cross section is a function of the magnitude of the magnetic moment (S) and the magnetic form factor (f_m) for the magnetic atom

$$p = 0.54Sf_m \times 10^{-12} \text{ cm}$$

and the magnetic interaction vector for the j^{th} atom depends on the unit vector (ε) for the scattering vector (**h**) and the unit vector for the magnetic moment on that atom($\mathbf{K}_j$)

$$\mathbf{q}_j = \varepsilon(\varepsilon\cdot\mathbf{K}_j)-\mathbf{K}_j$$

Magnetic structure factors and derivatives are calculated in **MAGSTRFCTR**.

Atom input and output in **GENLES** is handled by the subroutines **ATMSINP** and **ATMSOUT**, respectively. There are several atom editing routines all called by **EDTATM** in **EXPEDT**. The X-ray anomalous dispersion coefficients are edited as overall parameters by **EDTFFAC**.

Total Powder Diffraction Profile Intensity

The total normalized profile intensity, I_o, at any point in a powder diffraction pattern has contributions from the nearby reflections and from background scattering. The reflection contributions are calculated from the structure factors and are corrected for all geometric and sample dependent factors such as absorption, extinction, preferred orientation, etc. The background is modeled with a well behaved empirical function. The general expressions for the intensity of TOF data are

$$I_o = \frac{I'_o}{WI_i}$$

or for CW data

$$I_o = \frac{I'_o}{I_i}$$

and

$$I_c = I_b + S_h \sum_p S_{ph}Y_{ph}$$

where I'_o is the number of counts observed in a channel of width W, I_i is the incident intensity, I_b is the background value, S_h is the histogram scale factor, $S_{p,h}$ is the individual phase scale factor within an histogram and $Y_{p,h}$ is the contribution from the h^{th} reflection of the p^{th} phase. The two scale factors are useful for the analysis of multiphase mixtures. A weight, w, is assigned to each I_o from consideration of the variances in both I'_o and I_i. The sum is over those reflections from all phases in the sample that are sufficiently close to the profile point to make a significant contribution. Each of the terms in this expression will be discussed below. The computation of the total intensity and final assembly of its derivatives is done in subroutine **PDCALC**.

Incident Intensity Function

The incident intensity, I_i, for a time of flight (TOF) powder diffractometer can be measured by placing a null coherent scatterer such as vanadium in the normal sample position and then recording the spectrum observed by each of the counter banks. Alternatively, the incident spectrum can be obtained from a low efficiency beam monitor. Usually these spectra are used without correction for absorption or detector efficiency to determine the incident intensity. The lack of a detector efficiency correction in the neutron TOF case is exactly compensated because the powder diffraction data from a sample is collected with the same set of detectors. The lack of an absorption correction is compensated largely by the refinement of the sample absorption factor (see below). The incident intensity for a TOF diffractometer is represented by one of five possible functions each with a maximum of 11 or 12 coefficients. Only three of these functions are suitable for synchrotron x-rays; however, the usual procedure is to normalize synchrotron data point-by-point before processing by **GSAS** and not use the fitted incident intensity (see the section on **GSAS Standard Powder Data File**). These coefficients are determined by fitting to the measured incident spectrum; this is done by the program **FITSPEC**. It writes to an instrument parameter file the coefficients, estimated standard deviations (esd's) and the correlation matrix from a least squares fit. **POWPREF** uses this information to calculate the incident intensity and its esd for every point in a powder diffraction pattern. This esd is used to adjust the weight assigned to each profile point for the uncertainty in the calculated incident intensity.

The 'TYPE 1' function is a sum of exponentials of TOF (T) in milliseconds or 2Θ in degrees.

$$I_i = P_1 + P_2 e^{-(P_3 T)} + P_4 e^{-(P_5 T^2)} + \dots$$

This function has a maximum of 11 coefficients. The 'TYPE 2' function replaces the second term in the above function with a Maxwellian expression; again TOF is in milliseconds. This function is not suitable for x-rays.

$$I_i = P_1 + P_2 e^{-(P_3/T^2)}/T^5 + P_4 e^{-(P_5 * T^2)} + \dots$$

Again there is a maximum of 11 coefficients. The coefficient P_3 in this function and the 'TYPE 4' function shown below can be used to calculate an effective moderator temperature.

$$t = \frac{2.374\text{x}10^{-4}C^2}{P_3 sin 2\Theta}$$

where C is the diffractometer constant (DIFC). This temperature is usually 10-20K higher than the real temperature when the intensity data has not been corrected for absorption or detector efficiency. The 'TYPE 3' function is a 12 term Chebyschev polynomial of the first kind ("Handbook of Mathematical Functions," M. Abramowitz and I.A. Stegun, Eds., Ch. 22).

$$I_i = \sum_{j=1}^{12} P_j T'_{j-1}$$

where T'_{j-1} are the coefficients of the Chebyschev polynomial taken from Table 22.3, p 795 of the Handbook. Each coefficient is of the form

$$T'_n = \sum_{m=0}^{i-1} C_m X^m$$

and the values of C_m are listed in the Handbook. These coefficients are generated in subroutine **IFUNADV**. The TOF or 2Θ(T) is converted to X to make the Chebyschev polynomial orthogonal by

$$X = (2/T) - 1$$

Given that the usual range of TOF is 1 to 100 millisec and 2Θ is from 2° to 175° then X ranges from about -1 to +1 which is the orthogonal range for this function. The 'TYPE 4' incident intensity function has a Maxwellian term and part of the Chebyschev polynomial used for 'TYPE 3'. It is not used for x-rays.

$$I_i = P_1 + \frac{P_2}{T^5} e^{-(P_3/T^2)} + \sum_{j=4}^{12} P_j T'_{j-3}$$

Again T is TOF in milliseconds and T'_i are the coefficients of the Chebyschev polynomial of the first kind. The 'TYPE 5' function is the same as 'TYPE 3' except that X is defined as

$$X = T/10$$

The 'TYPE 3', 'TYPE 4' and 'TYPE 5' functions have a maximum of 12 coefficients. For constant wavelength data with no incident spectrum, a 'TYPE 0' incident spectrum is used and has no coefficients; this gives $I_i = 1.0$ for all data points and σI_o is taken only from I_o. The subroutine **HSTPROC** in **POWPREF** reads the incident spectrum parameters, computes the values by calling **INAWCAL** and places this information with the observed pattern on the histogram file. **INAWCAL** also provides the appropriate set of derivatives for use by **FITSPEC**. The histogram file is processed by **GENLES** using the subroutine **PDCALC**.

Background Functions

There are currently six background functions available in **GSAS** for fitting to powder diffraction data. Each function has a maximum of 36 possible coefficients although in vitrually all cases far fewer will suffice to fit the background in a powder pattern. In fact, an attempt to use a large number of background coefficients will usually fail in an unpredictable way. The first function is the 'Chebyschev polynomial of the first kind' and is similar to that used for the incident spectrum 'TYPE 3'. A conversion is applied it make the Chebyschev polynomial orthogonal:

$$X = \frac{2(T-T_{min})}{T_{max}-T_{min}} - 1$$

where T_{min} and T_{max} are the actual range of data used in the calculation. T is in milliseconds TOF or degrees 2Θ. Then the background intensity is calculated from

$$I_b = \sum_{j=1}^{36} B_j T'_{j-1}$$

The coefficients T'_j are the same as those for the 'TYPE 3' incident spectrum and the values of B_j are determined by least squares during the Rietveld refinement of the powder pattern. The second background function is a cosine Fourier series with a leading constant term.

$$I_b = B_1 + \sum_{j=2}^{36} B_j \cos\,(P(j-1))$$

In the case of CW data P is in degrees 2Θ and is just the detector position for the step. For TOF data the times are scaled by 180/TMAX, where TMAX is the maximum allowed by the incident spectrum. This function appears to be more robust than the Chebyschev function for both CW and TOF data and thus is chosen as the default.

The third function uses a straight line for the first part and the major features of a real space correlation function for the remainder. Thus this background function can model diffuse background from an amorphous phase in the sample or the background from a quartz sample holder. The function is

$$I_b = B_1 + B_2 T + \sum_{i=1}^{17} \frac{B_{2i+1} \sin\,(QB_{2i+2})}{QB_{2i+2}}$$

where

$$Q = 2\pi/d$$

The d-spacing is computed for each point from the TOF or 2Θ and the diffractometer constants (see below). The values of B_{2i+2} correspond to interatomic distances in the amorphous phase. To assist the user in estimating these values, **POWPLOT** has an option for plotting both the modified residuals and the correlation function from the profile deltas; the B_{2i+2} can be picked off the latter plot.

The fourth function is designed to account for background contributions that increase with Q. The principal contributor of this kind is thermal diffuse scattering so this function is an expansion of the exponential

$$I_b = \sum_{j=1}^{36} B_j \frac{Q^{2(j-1)}}{(j-1)!}$$

The fifth function accounts for background contributions that tend to rise at small Q. In x-ray scattering the principal contribution of this type is from air scatter in the vicinity of the sample. This function is assumed to be effectively the reciprocal of the previous one

$$I_b = \sum_{j=1}^{36} B_j \frac{(j-1)!}{Q^{2(j-1)}}$$

The sixth function is then a mixing of the previous two functions which can account for the background contributions at both low Q and high Q.

$$I_b = B_1 + \sum_{j=1}^{17} \left(B_{2j} \frac{Q^{2j}}{j!} + B_{2j+1} \frac{j!}{Q^{2j}} \right)$$

This function is generally useful for both x-ray and neutron powder data although it may require a few more terms to get a satisfactory fit to the background. All three of these latter functions use the same definition for Q that is used for the third function.

Except for function #3, these background functions are normally quite flat. There is usually only a slight curvature arising from the thermal diffuse scattering from the sample. Larger background contributions will be fitted by these functions given sufficient terms, but short period fluctuations not associated with an amorphous phase cannot be fit very well. In that case the fixed background subtraction feature of **GSAS** must be used for the fluctuating component of the background with the remainder fitted with one of these functions. Examples of background problems include frame overlap peaks in a TOF pattern, miscellaneous peaks from sources outside the experiment and unaccounted extra phases. In the case of extra Bragg peaks from other phases in the sample, it is better to insert the phase explicitly and fit it as part of the crystallographic model. Using too many background terms may seriously degrade the quality of some other parts of the least squares model. In particular refinement of atom thermal parameters and some profile shape parameters may become very unsatisfactory because a very complex background function may begin to model parts of the Bragg peak intensities. Thus it is best to use the minimum number of background terms that give a satisfactory fit. The background coefficients are edited by subroutine **EDTBAK** and the input, output and calculations in **GENLES** are done by **BACKINP**, **BACKOUT** and **BACKCAL**, respectively. The routine **CALCBAK** is used in **POWPLOT** for subtracting calculated background.

Bragg Intensity - $Y_{p,h}$

The contributed intensity, $Y_{p,h}$, from a Bragg peak to a particular profile intensity will depend on several things. Obviously the value of the structure factor and the amount of that particular phase will determine the total contribution. In addition, the peak shape and width in relation to its position will also have an effect. The intensity is also affected by extinction and absorption as well as some geometric factors.

$$Y_{p,h} = F^2_{p,h} H(T-T_{p,h}) K_{p,h}$$

where $F_{p,h}$ is the structure factor for a particular reflection, $H(T-T_{p,h})$ is the value of the profile peak shape function for that reflection at a position, T, displaced from its expected position, $T_{p,h}$, and $K_{p,h}$ is the product of the various geometric and other correction factors for that reflection. In **GSAS** all of the applicable correction factors are applied to the Bragg intensities so that the resulting scale factors are proportional to the number of unit cells of each phase present in the sample. Moreover, the corrections include the angular effects to produce scale factors in a TOF experiment that are independent of scattering angle. The reflection position independent information and associated derivatives for powder data are assembled by subroutine **REFLIN** and written to a 'window' array which is read by **PDCALC** as the profile points are processed.

Intensity Correction Factors

The intensity correction factors, $K_{p,h}$, consist of those factors which are dependent on the sample, the instrument geometry, and the type of radiation used.

$$K_{p,h} = E_{p,h}A_hO_{p,h}M_pL/V_p$$

where $E_{p,h}$ is an extinction correction, A_h is an absorption correction, $O_{p,h}$ is the preferred orientation correction, M_p is the reflection multiplicity, L is the angle dependent correction (Lorentz-polarization), and V_p is the unit cell volume for the phase. These corrections and their derivatives are assembled in **REFLIN** and are dependent only on the reflection. Each will be discussed in turn below.

Extinction in Powders

The extinction in powders is calculated according to a formalism developed by Sabine, Von Dreele and Jorgensen (T.M. Sabine, Aust. J. Phys., 1985, 38, 507-18 & T.M. Sabine, R.B. Von Dreele & J.-E. Jorgensen, Acta Cryst A44, 374-379, 1988) and is a primary extinction effect within the crystal grains. The extinction correction $E_{p,h}$ is a combination of Bragg and Laue components

$$E_{p,h} = E_b \sin^2\Theta + E_l \cos^2\Theta$$

where

$$E_b = 1/\sqrt{1+x}$$

and

$$E_l = 1 - \frac{x}{2} + \frac{x^2}{4} - \frac{5x^3}{48} \ldots \text{ for } x < 1$$

or

$$E_l = \sqrt{\frac{2}{\pi x}}\left[1 - \frac{1}{8x} - \frac{3}{128x^2} - \frac{15}{1024x^3} \ldots\right] \text{ for } x > 1$$

where

$$x = E_x(\lambda F/V)^2$$

where F is the calculated structure factor and V is the unit cell volume. The units for these expressions are such that E_x is in μm^2 and is a direct measure of the mosaic block size in the powder sample. There is a value of the coefficient E_x for each phase in each histogram in a powder mixture. The powder extinction coefficients are input and output by **EXTPINP** and **EXTPOUT**, respectively; the function and its derivative are calculated by **EXTPCAL**. Editing is done in **EDTEXTP**.

Powder Absorption Factor

Several powder absorption functions are available in **GSAS**. In the first one, the absorption, A_h, for a cylindrical sample is calculated for powder data according to an empirical formula (A.W. Hewat, Acta Cryst., A35, 248, 1979 & K.D. Rouse, M.J. Cooper, & A. Chakera, Acta Cryst., A26, 682-691, 1970). It is assumed for TOF data that the linear absorption of all components in the sample vary with 1/velocity, and it is indistinguishable from multiple scattering effects within the sample. For constant wavelength data the absorption coefficient, A_B, is related to the value for 1Å neutrons; the correction is indistinguishable from thermal motion effects and should not be refined. For X-ray data it is suitable only for data taken in the Debye-Scherrer geometry on a weak absorber; it should not be used for Bragg-Bretano or other flat plate geometries.

$$A_h = e^{(-T_1 A_B \lambda - T_2 A_B{}^2 \lambda^2)}$$

where

$$T_1 = 1.7133 - 0.0368 \sin^2\Theta$$

and

$$T_2 = -0.0927 - 0.3750 \sin^2\Theta$$

The second function is a simple linear absorption which is useful for the neutron case where the beam suffers substantial absorption by passing through sample containment vessels, etc.

$$A_h = e^{-A_B \lambda}$$

The third and fourth absorption functions are two forms for the surface roughness effect that is prevalent in Bragg-Brentano x-ray diffraction geometry. These two functions have two refinable coefficients, A_{B1} and A_{B2}. Surface roughness can strongly reduce the intensity of Bragg reflections at low scattering angles and is caused by a gradient in the sample packing density as a function of depth. Samples with high absorption are more susceptible to surface roughness effects and if not corrected can yield negative temperature factors in the crystal structure results. Function three is a "normalized" form of the function described by Pitschke, Hermann and Mattern (Powder Diffraction, 8,74-83, 1993).

$$A_h = \frac{1 - A_{B1}(1/\sin\Theta - A_{B2}/\sin^2\Theta)}{1 - A_{B1} + A_{B1}A_{B2}}$$

Function four is a normalized form of the empirical function proposed by Suortti (J. Appl. Cryst. 5, 325-331, 1972).

$$A_h = \frac{A_{B1}+(1-A_{B1})e^{-A_{B2}/sin\Theta}}{A_{B1}+(1-A_{B1})e^{-A_{B2}}}$$

The two surface roughness functions give essentially identical results, however, the Suortti function is better behaved at low (<20° 2Θ) scattering angles.

The absorption coefficients are input and output by **ABSCINP** and **ABSCOUT**, respectively; the function and derivative are calculated by **ABSCCAL**. Editing is performed by **EDTABS**.

Preferred Orientation of Powders

The preferred orientation correction, $O_{p,h}$, is the formulation of Dollase and March (Dollase, W.A. (1986). J. Appl. Cryst. 19, 267-272 and March, A. (1932). Z. Kristallogr. 81, 285-297). It is applicable for both needle and plate shaped crystals and is explicitly correct when the sample has cylindrical symmetry along the diffraction vector and is a reasonable approximation when the cylinder axis is perpendicular to the diffraction plane. Thus, it covers the two most common diffraction geometries for powder diffraction; Debye-Scherrer geometry as used in neutron diffraction and Bragg-Bretano geometry as used for most X-ray powder diffractometers. It is especially effective when the sample is rotated about the appropriate axis to ensure cylindrical symmetry. The refinable coefficient, R_o, gives the effective sample compression or extension along the cylinder axis due to preferred orientation. If there is no preferred orientation then R_o=1.0.

$$O_{p,h} = \sum_{j=1}^{n}(R_o^2 cos^2 A_j + sin^2 A_j/R_o)^{-3/2}/M_p)$$

where A_j is the angle between the preferred orientation axis and the reflection vector h_p. The sum is over the reflections equivalent to h_p. It is assumed that the preferred orientation axis for the sample lies either preferentially normal to the diffraction plane or coincident with the diffraction vector. The value of the coefficient will depend on both the diffraction geometry and the crystallite shape. If a cylindrical sample is used so that platy crystals would be expected to pack normal to the diffraction plane R_o will be greater than one. For a flat plate sample, platy crystals are expected to pack normal to the diffraction vector and R_o will be less than one. For needle-shaped crystals the reverse relationships for the value of R_o are obtained. A second form for the preferred orientation correction uses the March-Dollase formulation for a cylindrically symmetric distribution which is oriented to be parallel to the incident beam. For both functions, it is possible to define a set of multiple preferred orientations for each phase. Thus, each orientation has two coefficients, R_o and f_o; f_o is the fraction of crystallites that are associated with a particular orientation axis. The values of f_o are forced to sum to 1.0. The routines for input, output and calculation are **PRFOINP**, **PRFOOUT** and **PRFOCAL**, respectively. The editing is done by **EDTPRFO** and has facilities for selection of the preferred orientation axes as well as editing the coefficient and refinement flag.

Reflection Multiplicity

The reflection multiplicity, M_p, as determined by symmetry is computed when the reflection set is generated by **POWPREF** and is written on the reflection file along with the Miller indices and other relevant values associated with each reflection. The reflection generation is done by **REFGEN** and **REFGEN1** which produces the unique, space group allowed set of reflections for all possible 3-dimensional space groups.

Angle Dependent Corrections

The angle dependent corrections for powder diffraction include the Lorentz factor for both neutrons and x-rays and the polarization factor for x-rays. For TOF neutron data there is an additional factor for the variation of scattered intensity with wavelength. For TOF neutrons

$$L = d^4 \sin\Theta$$

for constant wavelength neutrons

$$L = \frac{1}{2\sin^2\Theta\cos\Theta}$$

and for x-rays there are three functions. The first is

$$L = \frac{P_h+(1-P_h)\cos^2 2\Theta}{2\sin^2\Theta\cos\Theta}$$

the second is suitable for x-ray diffractometers with an incident beam monochromator in parallel geometry

$$L = \frac{P_h\cos^2 2\Theta+1}{\sin^2\Theta\cos\Theta}$$

and the third is for a diffracted beam monochromator also in parallel geometry

$$L = \frac{1+P_h\cos^2 2\Theta}{(1+\cos^2 2\Theta)\sin^2\Theta\cos\Theta}$$

where P_h is a refinable polarization fraction defined for each x-ray powder histogram. These terms are calculated in **DIFSCAL**.

Profile Peak Shape Function

The contribution a given reflection makes to the total profile intensity depends on the shape function for that reflection profile, its width coefficients and the displacement of the peak from the profile position. The locations of the peak are given in microseconds of TOF or in centidegrees 2Θ. Discussion of these values is given first followed by details of the peak shape functions presently installed in **GSAS**.

Neutron Time of Flight

For a neutron time-of-flight powder diffractometer the relationship between the d-spacing for a particular powder line and its TOF is

$$T_{p,h} = \mathrm{DIFC}\ d_p + \mathrm{DIFA}\ d^2_p + \mathrm{ZERO}.$$

The three parameters DIFC, DIFA and ZERO are characteristic of a given counter bank on a TOF powder diffractometer. The values of these constants as used in **GSAS** yield TOF in μsec. DIFC may be calculated with good precision from the flight paths, diffraction angle, and counter tube height by use of the de Broglie equation.

$$\mathrm{DIFC} = 252.816 \cdot 2\mathit{sin}\Theta\left(L_1+\sqrt{L_2^2+L_3^2/16}\,\right)$$

where Θ is the Bragg angle, L_1 is the primary flight path, L_2 is sample to detector center distance and L_3 is the height of the detector; all distances are in meters. The units of DIFC are then μsec/Å. These coefficients are also slightly affected by the choice of profile function (see below). Precise values for constants DIFC, DIFA and ZERO must be obtained by fitting to a powder diffraction pattern of a standard material; this facility is available in **GSAS**. These coefficients are read by **GENLES** in subroutine **DIFSINP**, they are output by **DIFSOUT** and the calculation of the functions and derivatives is done by **DIFSCAL**. They are edited by subroutine **EDTDIF** in **EXPEDT**.

Neutron and X-ray 2Θ

The reflection position in a constant wavelength experiment is obtained from Bragg's Law.

$$\lambda = 2d_p \mathit{sin}\ \Theta$$

where λ is the wavelength. In **GSAS** the powder diffraction profile positions are in centidegrees 2Θ. Thus, the expression for the reflection position is

$$T_{p,h} = 200\mathit{asin}\ (\lambda_h/2d_p) + \mathrm{ZERO}$$

In the case of neutron diffraction the **GSAS** system requires a single value for λ_h (called LAM1 in the code) and the ZERO value. This value of λ_h is obtained by fitting the powder pattern of a standard having a well known set of lattice parameters. For x-rays two values of λ_h can be used (called LAM1 and LAM2) along with the ZERO value. For conventional sources these wavelengths are well known and are tabulated in many references; however for synchrotron sources a calibration of the single wavelength with a standard sample can be performed. If both LAM1 and LAM2 are present they can not be refined. The intensity associated with LAM2 is normally assumed to be 1/2 the intensity of LAM1 in accord with theoretical expectations for K x-ray radiation emission from a laboratory source. However, this ratio (called KRATIO) can also be refined for those cases where the instrument optics have modified the $K\alpha_2/K\alpha_1$ ratio. The same routines in **EXPEDT** and **GENLES** that handle the TOF instrument parameters DIFC, DIFA and ZERO also handle LAM1, LAM2 and KRATIO.

Profile Functions

Each type of powder diffraction data has its own set of profile functions, $H[T-T_{p,h}]$; currently there are a small number installed in **GSAS** for each type of histogram which are discussed in turn. In all cases the input and output of the profile coefficients are done by **PRFCINP** and **PRFCOUT**, respectively. The calculations are grouped together in **PRFCCAL** which calls specific routines for each function. The editing is handled by **EDTPRF** which calls routines specific to the powder data type.

TOF Profile Functions

There are currently three TOF profile functions installed in **GSAS**. The first one is the function (J.D. Jorgensen, D.H. Johnson, M.H. Mueller, J.G. Worlton & R.B. Von Dreele, Proc. Conf. on Diffraction Profile Analysis, Cracow, 14-15 Aug., 1978, 20-22; R.B. Von Dreele, J.D. Jorgensen & C.G. Windsor, J. Appl. Cryst., 15 581-589, 1982; R.B. Von Dreele, unpublished).

$$H(\Delta T) = N[e^{u} erfc\,(y) + e^{v} erfc\,(z)]$$

where ΔT is the difference in TOF between the reflection position, $T_{p,h}$, and the profile point, T; the terms N,u,v,y and z are dependent on the profile coefficients. The function *erfc* is the complementary error function (see "Handbook of Mathematical Functions," Ch. 7). This profile function is the result of convoluting two back-to-back exponentials with a Gaussian.

$$H(\Delta T) = \int G(\Delta T-\tau)E(\tau)d\tau$$

where

$$E(\tau) = 2Ne^{\alpha\tau} \text{ for } \tau < 0$$

and

$$E(\tau) = 2Ne^{-\beta\tau} \text{ for } \tau > 0$$

for the two exponentials; α and β are the rise and decay coefficients for the exponentials. The Gaussian function is

$$G(\Delta T-\tau) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(\Delta T-\tau)^2/2\sigma^2}$$

The Gaussian variance is the coefficient σ^2. These functions when convoluted give the profile function shown above. The normalization factor, N, is

$$N = \frac{\alpha\beta}{2(\alpha + \beta)}$$

The coefficients u,v,y and z are

$$u = \frac{\alpha}{2}(\alpha\sigma^2 + 2\Delta T)$$

$$v = \frac{\beta}{2}(\beta\sigma^2 - 2\Delta T)$$

$$y = \frac{\alpha\sigma^2 + \Delta T}{\sqrt{2\sigma^2}}$$

$$z = \frac{\beta\sigma^2 - \Delta T}{\sqrt{2\sigma^2}}$$

Each of the three coefficients α, β and σ^2 all show specific dependence on the reflection d-spacing. In the case of σ^2 there are terms for anisotropic broadening that depend on the angle ϕ between h_p and a broadening axis.

$$\alpha = \alpha_o + \alpha_1/d$$

$$\beta = \beta_o + \beta_1/d^4$$

$$\sigma^2 = \sigma_o^2 + \sigma_1^2 d^2 + \sigma_2^2 d^4 + (\sigma_{oe}^2 + \sigma_{1e}^2 d^2 + \sigma_{2e}^2 d^4)\cos^2\phi$$

In addition, the ΔT is modified to accomodate the isotropic, ε_i, and anisotropic, ε_a, strain induced displacement of the diffraction lines from their positions expected from the lattice parameters by

$$\Delta T = (T - T_{p,h}) - \varepsilon_i d - \varepsilon_a d \cos\phi$$

Thus the profile function has twelve coefficients (α_o, α_1, β_o, β_1, σ_o^2, σ_1^2, σ_2^2, σ_{oe}^2, σ_{1e}^2, σ_{2e}^2, ε_i and ε_a) which are refinable by **GENLES**. Within **GSAS** these parameters are named "alp-0", "alp-1", "bet-0", "bet-1", "sig-0", "sig-1", "sig-2", "s0ec", "s1ec", "s2ec", "rstr" and "rsta", respectively. These parameters are sensitive to the scattering angle and any possible sample broadening effects; there is a set of these for each phase and each powder pattern.

The second TOF profile function has been developed by W.I.F. David and R.B. Von Dreele (unpublished) and incorporates the moderator pulse shape of S. Ikeda & J.M. Carpenter, Nuc. Inst. and Meth., A239, 1985, 536-544. The Ikeda-Carpenter function is composed of a convolution of two functions; the first represents the slowing down spectrum from the moderator

$$S_k(\tau) = \frac{\alpha^3}{2}\tau^2 e^{-\alpha\tau}$$

and the second is a mixing of a δ-function and an exponential decay:

$$R_k(\tau) = (1-R)\,\delta(\tau) + Re^{-\beta\tau}$$

The two parts describe the leakage of fast and slow neutrons from the moderator and have 'fast' and 'slow' decay constants, α and β, respectively, which are related to the moderator material and dimensions. The mixing coefficient, R, is related to the moderator temperature. The result of the convolution is

$$I_k(t) = \int S_k(\tau)R_k(t-\tau)d\tau$$

$$I_k(t) = \frac{\alpha^3}{2}\left[(1-R)t^2 e^{-\alpha t} + \frac{2\beta R}{(\alpha-\beta)^3}\left\{e^{-\beta t} - \left[1 + t(\alpha-\beta) + \frac{t^2}{2}(\alpha-\beta)^2\right]e^{-\alpha t}\right\}\right]$$

In **GSAS** an alternative form of this function is used to simplify some of the mathematics

$$I_k(t) = (1-R)\frac{\alpha(1-k^2)}{2k^2}\left[e^{-\alpha t(1-k)} + e^{-\alpha t(1+k)} - 2e^{-\alpha t}\right] + \frac{R\alpha\beta(1-k^2)}{2k^2}\left[\frac{2\alpha^2k^2}{xyz}e^{-\beta t} - \frac{1}{z}e^{-\alpha t(1+k)} - \frac{1}{x}e^{-\alpha t(1+k)} + \frac{2}{y}e^{-\alpha t}\right]$$

Where k is a perturbation coefficient (=0.05 in **GSAS**) and

$x = \alpha(1-k)-\beta$

$y = \alpha-\beta$

$z = \alpha(1+k)-\beta$

This function is convoluted with a pseudo-Voigt to give the full peak shape function

$$H(\Delta T) = \int P(\Delta T-t)I_k(t)dt$$

The pseudo-Voigt is defined as a linear combination of a Lorentzian and a Gaussian

$$P(t) = \eta L(t,\Gamma) + (1-\eta)G(t,\Gamma)$$

The Gaussian function is defined above and the Lorentzian function is

$$L(t) = \frac{\Gamma}{2\pi}\left[\frac{1}{(\Gamma/2)^2 + t^2}\right]$$

The mixing factor, η, is given by P. Thompson, D.E. Cox & J.B. Hastings, J. Appl. Cryst.,20,79-83, 1987 as a function of the total FWHM (Γ) and the Lorentzian coefficient (γ)

$$\eta = 1.36603(\gamma/\Gamma) - 0.47719(\gamma/\Gamma)^2 + 0.11116(\gamma/\Gamma)^3$$

where Γ is a function of the Gaussian FWHM (Γ_g) and γ

$$\Gamma = \sqrt[5]{\Gamma_g^5 + 2.69269\,\Gamma_g^4\gamma + 2.42843\,\Gamma_g^3\gamma^2 + 4.47163\,\Gamma_g^2\gamma^3 + 0.07842\,\Gamma_g\gamma^4 + \gamma^5}$$

and the Gaussian FWHM is

$$\Gamma_g = \sqrt{8\sigma^2 \mathit{ln}\ 2}$$

Thus the two convolutions between the Ikeda-Carpenter function and a Gaussian and Lorentzian are needed. The Gaussian part is

$$G'(\Delta T) = \int G(\Delta T\text{-}t)I_k(t)dt$$

or

$$G'(\Delta t) = \frac{\alpha(1-k^2)}{4k^2}\left[\frac{2R\alpha^2\beta k^2}{xyz}h(g,r) + \left\{1 - \frac{R\alpha(1+k)}{z}\right\}h(g,v) + \left\{1 - \frac{R\alpha(1-k)}{x}\right\}h(g,u) - 2\left\{1 - \frac{R\alpha}{y}\right\}h(g,s)\right]$$

and

$$h(g,r) = e^{(g+r^2)}\mathit{erfc}\ (r)$$

where

$$g = \frac{-\Delta T^2}{2\sigma^2}$$

$$r = \frac{\beta\sigma^2-\Delta T}{\sigma\sqrt{2}} \qquad s = \frac{\alpha\sigma^2-\Delta T}{\sigma\sqrt{2}}$$

$$u = \frac{\alpha(1-k)-\Delta T}{\sigma\sqrt{2}} \qquad v = \frac{\alpha(1+k)-\Delta T}{\sigma\sqrt{2}}$$

The Lorentzian part is also obtained by integration

$$L'(\Delta T) = \int L(\Delta T\text{-}t)I_k(t)dt$$

or

$$L'(\Delta T) = \frac{\alpha(1-k^2)}{2\pi k^2 xyz}\left[2R\alpha^2\beta k^2 I(q) + yz\{x-R\alpha(1-k)\}I(p(1-k)) + xy\{z-R\alpha(1+k)\}I(p(1+k)) - 2xz\{y-R\alpha\}I(p)\right]$$

where

$I(q) = \mathrm{Im}[e^{q}E_1(q)]$ (i.e. imaginary part of e^{q} times the exponential integral of q)

and

$p = -\alpha\Delta T + \frac{i\alpha\gamma}{2} \qquad q = -\beta\Delta T + \frac{i\beta\gamma}{2}$

The profile coefficients are defined by

$$\alpha = \frac{1}{\alpha_o + \alpha_1\lambda}$$

$$\beta = 1/\beta_o$$

$$R = e^{-(81.799/\kappa\lambda^2)}$$

$$\sigma^2 = \sigma_o{}^2 + \sigma_1{}^2 d^2 + \sigma_2{}^2 d^4$$

$$\gamma = \gamma_o + \gamma_1 d + \gamma_2 d^2 + (\gamma_{1e} d + \gamma_{2e} d^2) \cos\phi$$

This function currently has 15 parameters (α_o, α_1, β_o, κ, $\sigma_o{}^2$, $\sigma_1{}^2$, $\sigma_2{}^2$, γ_o, γ_1, γ_2, γ_{1e}, γ_{2e}, DIFC, DIFA and ZERO) and is still under development. DIFC is included to compensate for the offset in the peak location from that used for the first and third TOF functions. In this function the peak location is where the Ikeda-Carpenter function first rises from zero, i.e. at the front base of the profile. The other functions have the peak location at the junction between the exponentials, i.e. just to the low TOF side of the peak top. A weakness of this function is that it only suitable for data taken with very short detectors. Usually the detector banks are made up of a rank of ^{3}He tubes which are 6-12" long and the peak profile displays a sharp rise from the geometric effects from this tube length. The names of these coefficients within **GSAS** are "alp-0", "alp-1", "beta", "switch", "sig-0", "sig-1", "sig-2", "gam-0", "gam-1", "gam-2", "stec", "ptec", "difc", "difa", and "zero", respectively.

The third TOF profile function is an extension of the first function to include the generally Lorentzian broadening exhibited by most samples. Thus, the anisotropic broadening terms have been assumed to be Lorentzian. It is a convolution of the back-to-back exponentials used in the first function with the pseudo-Voigt used in the second function.

$$H(\Delta T) = \int E(\Delta T - t)P(t)dt$$

$$H(\Delta T) = (1-\eta)N[e^{u} erfc(y) + e^{v} erfc(z)] + \frac{2N\eta}{\pi}\{-\mathrm{Im}[e^{p}E_1(p)] - \mathrm{Im}[e^{q}E_1(q)]\}$$

where N, u, v, y and z are defined as in the first function and p, q and η are defined as in the second function. The profile coefficients α, β and σ^2 are defined in ways similar to the two previous functions

$$\alpha = \alpha_1/d$$

$$\beta = \beta_o + \beta_1/d^4$$

$$\sigma^2 = \sigma_o{}^2 + \sigma_1{}^2 d^2 + \sigma_2{}^2 d^4$$

For the γ profile coefficient an additional type of broadening is introduced where two classes of reflections can be defined. Those that fall on a sublattice (as defined by three vectors) have the following expression for the γ coefficient

$$\gamma = \gamma_o + \gamma_1 d + \gamma_2 d^2 + (\gamma_{1e} d + \gamma_{2e} d^2)\mathit{cos}\ \phi$$

while the rest have the following expression (note the difference in the last coefficient between these two equations)

$$\gamma = \gamma_o + \gamma_1 d + \gamma_2 d^2 + (\gamma_{1e} d + \gamma_{2s} d^2)\mathit{cos}\ \phi$$

This means that one set of reflections has a different particle size anisotropy than the other set. This effect is seen when the sample contains stacking faults which will broaden some reflections leaving a sublattice of sharp reflections which correspond to the substructure which continues unmodified through the stacking fault. Generally, γ_{2s} will be much larger than γ_{2e}. The sublattice is defined by three vectors chosen by the user via the profile function **'A'** option in **EDTPRF**. Thus, this function has 13 coefficients (α_1, β_o, β_1, σ_o^2, σ_1^2, σ_2^2, γ_o, γ_1, γ_2, γ_{2s}, γ_{1e}, γ_{2e}, ε_i and ε_a). These are named "alp", "bet-0", "bet-1", "sig-0", "sig-1", "sig-2", "gam-0", "gam-1", "gam-2", "gsf", "g1ec", "g2ec", "rstr", and "rsta", respectively, within **GSAS**.

The editing of the coefficients for all three functions is done by **EDTPTP1**. Calculations are handled through **PRFCCAL** which calls **EXPGAUS**, **IKCARVT** and **EXPSTVGT** for the three functions, respectively.

Interpretation of TOF Powder Profile Coefficients

The profile coefficients from a time of flight (TOF) neutron powder pattern Rietveld refinement with **GSAS** can give information about the microtexture of the sample. This discussion will describe how this information can be extracted from the coefficients.

Strain broadening

In the reciprocal space associated with a sample with isotropic strain, there is a broadening of each point which is proportional to the distance of the point from the origin, i.e.

$$\Delta d^*/d^* = \text{constant}$$

In real space (the regime of a TOF experiment) then

$$\Delta d/d = \text{constant}$$

for strain broadening. Thus examination of the expression for the Gaussian variance of the peak shape from a TOF pattern for the first function

$$\sigma^2 = \sigma_o^2 + \sigma_1^2 d^2 + \sigma_2^2 d^4 + (\sigma_{oe}^2 + \sigma_{1e}^2 d^2 + \sigma_{2e}^2 d^4)\mathit{cos}\ ^2\phi$$

implies that the second term contains an isotropic contribution from strain broadening. The other major contribution to σ_1^2 is from the instrument; because it is expressed as a variance, it can simply be subtracted. The remainder is then converted to give strain (S) as a dimensionless value which is frequently expressed as percent strain or fractional strain as a full width at half maximum.

$$S = \frac{1}{C}\sqrt{8\ln 2(\sigma_1^2 - \sigma_{1i}^2)}\ 100\%$$

where C is the diffractometer constant (DIFC) that relates TOF to d-spacing and σ_{1i}^2 is the instrumental contribution. In the case of anisotropic strain broadening, the parallel component of the strain is calculated from

$$S_{\parallel} = \frac{1}{C}\sqrt{8\ln 2(\sigma_1^2 + \sigma_{1e}^2 - \sigma_{1i}^2)}\ 100\%$$

The perpendicular component is then

$$S_{\perp} = \frac{1}{C}\sqrt{8\ln 2(\sigma_1^2 - \sigma_{1i}^2)}\ 100\%$$

For the second and third functions, the sample broadening is assumed to be Lorentzian and examination of the expression

$$\gamma = \gamma_o + \gamma_1 d + \gamma_2 d^2 + (\gamma_{1e} d + \gamma_{2e} d^2)\cos\phi$$

indicates that strain should affect the second term. We assume that the instrumental contribution is Gaussian so no correction for an instrumental contribution is needed here

$$S = \frac{1}{C}\gamma_1\ 100\%$$

As above, the anisotropic strain can be determined from the two expressions

$$S_{\parallel} = \frac{1}{C}(\gamma_1 + \gamma_{1e})\ 100\%$$

$$S_{\perp} = \frac{1}{C}\gamma_1\ 100\%$$

Particle size broadening

In reciprocal space isotropic particle size broadening makes all points the same size independent of the distance from the origin. Thus,

$$\Delta d^* = \text{constant}$$

The reciprocal of this quantity is then the average particle size. In real space (for TOF) the broadening is

$$\Delta d/d^2 = \text{constant}$$

From the expression for the Gaussian broadening of a TOF peak for the first function, the particle size affects the third term (σ_2^2) in the expression. This term generally has no instrument contribution and is used directly to calculate the particle size. Since it is in $\mu\text{sec}^2/\text{Å}^2$ and is a variance, the particle size (p) then is given by

$$p = \frac{CK}{\sqrt{8 \mathit{ln}\, 2\sigma_2^2}}$$

where C is the diffractometer constant (DIFC), K is the Scherrer constant and the units for p are Å. The anisotropy in the particle size can also be determined relative to the broadening axis so that the parallel component is

$$p_{\parallel} = \frac{CK}{\sqrt{8 \mathit{ln}\, 2(\sigma_2^2 + \sigma_{2e}^2)}}$$

and the perpendicular component is

$$p_{\perp} = \frac{CK}{\sqrt{8 \mathit{ln}\, 2\sigma_2^2}}$$

For the second and third functions, the corresponding Lorentzian particle size broadening appears in the third term so the particle size is

$$p = \frac{CK}{\gamma_2}$$

The anisotropy is then given by

$$p_{\parallel} = \frac{CK}{\gamma_2 + \gamma_{2e}}$$

$$p_{\perp} = \frac{CK}{\gamma_2}$$

In the presence of stacking faults, the γ_{2s} coefficient can be used to obtain the average distance between faults by

$$p_s = \frac{C}{\gamma_{2s}}$$

where the fault planes are perpendicular to the broadening axis.

As was noted for the strain, it has usually been observed that the particle size broadening is Lorentzian. Thus, it would appear that the third function would best fit diffraction data taken on high resolution TOF diffractometers with tall detectors.

CW Profile Functions

There are currently just two CW profile functions which are available for both x-rays and neutrons. The first function installed in **GSAS** is to be used for low resolution constant wavelength neutron powder diffraction data and is the standard Gaussian function modified for peak asymmetry, A_s, as described by Rietveld and others (H.M. Rietveld, J. Appl.

Cryst., 2, 65-71, 1969; Cooper & Sayer, J. Appl. Cryst., 8, 615-618, 1975; & Thomas, J. Appl. Cryst., 10, 12-13, 1977).

$$H(\Delta T) = N[1 - \Delta T'|\Delta T'|A_s/\tan\Theta]e^{-\Delta T'^2/2\sigma^2}$$

the normalization factor, N, is

$$N = 1/\sqrt{2\pi\sigma^2}$$

and the modified 2Θ difference is

$$\Delta T' = \Delta T + F_1/\tan 2\Theta$$

The variance of the peak, σ^2, varies with 2Θ as

$$\sigma^2 = U\tan^2\Theta + V\tan\Theta + W + F_2/\tan^4\Theta$$

Thus there are six profile coefficients U, V, W, A_s, F_1 & F_2 for constant wavelength neutron data; these are named "U", "V", "W", "asym", "F1", and "F2", respectively in **GSAS**. This function and its derivatives are calculated in **MODGAUS**, the coefficients are edited by **EDTPTP2**.

The second and considerably more successful function employs a multi-term Simpson's rule integration described by C.J. Howard (J. Appl. Cryst.,15, 615-620, 1982) of the pseudo-Voigt, F(ΔT), described by Thompson, et al. and used above in the second and third functions for TOF data.

$$H(\Delta T) = \sum_{i=1}^{n} g_i F(\Delta T')$$

where the pseudo-Voigt is

$$F(\Delta T) = \eta L(\Delta T',\Gamma) + (1-\eta)G(\Delta T',\Gamma)$$

The mixing coefficient, η, and the FWHM, Γ, are defined above. The 2Θ difference modified for asymmetry, A_s, and sample shift, S_s, is

$$\Delta T' = \Delta T + f_i A_s/\tan 2\Theta + S_s\cos\Theta + T_s\sin 2\Theta$$

where the number of terms in the sum depends on the size of A_s. The corresponding Simpson's rule coefficients, g_i and f_i, depend on the number of terms in the summation. In the case of Bragg-Bretano geometry for x-ray powder diffraction, the sample shift in can be interpreted as a physical shift of the sample, s, from the diffractometer axis by

$$s = \frac{-\pi R S_s}{36000}$$

where R is the diffractometer radius. In a similar way, the effective sample absorption can be obtained from the transparency coefficient, T_s, by

$$\mu_{eff} = \frac{-9000}{RT_s\pi}$$

The variance of the peak, σ^2, varies with 2Θ as

$$\sigma^2 = U\tan^2\Theta + V\tan\Theta + W + P/\cos^2\Theta$$

where U, V and W are the coefficients described by Cagliotti, Pauletti and Ricci in 1958 (Nucl. Instrum.,**3**, 223) and P is the Scherrer coefficient for Gaussian broadening. The Lorentzian coefficient, γ, varies as

$$\gamma = (X + X_e\cos\phi)/\cos\Theta + (Y + Y_e\cos\phi)\tan\Theta$$

The first term is the Lorentzian Scherrer broadening and includes an anisotropy coefficient, X_e. The second term describes strain broadening and also includes an anisotropy coefficient. If a sublattice is defined by use of "stacking fault vectors", then the above function only is applied to the reflections that are part of the sublattice. All other reflections have their Lorentzian broadening defined by (note the change from X_e to X_s)

$$\gamma = (X + X_s\cos\phi)/\cos\Theta + (Y + Y_e\cos\phi)\tan\Theta$$

This function gives the different anisotropic Scherrer broadening that is associated with the presence of stacking faults and is similar to that used in the #2 and #3 TOF functions shown above.

Thus there are twelve coefficients for this function (U, V, W, X, Y, T_s, A_s, S_s, P, X_e, Y_e and X_s). Within **GSAS** these are named "GU", "GV", "GW", "LX", "LY", "trns", "asym", "shft", "GP", "stec", "ptec", and "sfec", respectively. This function gives a better fit to asymmetric profiles than the first one and shows less correlation with the lattice parameters. The function and its derivatives are generated by **SIMGAUS**. The editing of the coefficients for these functions for neutron data are done in **EDTPTP2**. The coefficients for x-ray data are edited by **EDTPTP3**. The pairs of peaks arising from the $\alpha1$-$\alpha2$ doublet in the conventional x-ray case are treated as separate reflections.

Interpretation of CW Powder Profile Coefficients

As was the case for the TOF profile functions, the coefficients from a CW powder profile function can also be interpreted to give both strain and particle size information. Because the first function is suitable only for low resolution neutron CW diffractometers, it will rarely yield any significant line broadening information. Thus, the following discussion will consider only the coefficients from the second CW function.

Strain broadening

In the case of a CW experiment the strain broadening in real space is related to 2Θ broadening from

$$\Delta d/d = \Delta 2\Theta \cot\Theta = \text{constant}$$

or

$$\Delta 2\Theta = (\Delta d/d)\tan\Theta$$

In this expression $\Delta 2\Theta$ is in radians. Examination of the expression for the Gaussian broadening

$$\sigma^2 = U\tan^2\Theta + V\tan\Theta + W + P/\cos^2\Theta$$

indicates that the first term contains a strain broadening component. As for the TOF expression, this is a variance and the instrument contribution can be subtracted off. This variance is in centideg^2 and must be converted to radians to yield strain, thus

$$S = \frac{\pi}{18000}\sqrt{8\ln 2(U - U_i)}\ 100\%$$

Alternatively, the Lorentzian component of a CW peak shape has the expression

$$\gamma = (X + X_e\cos\phi)/\cos\Theta + (Y + Y_e\cos\phi)\tan\Theta$$

and the strain term is the one that varies with $\tan\Theta$. Again any instrumental or spectral contribution can be subtracted to yield the strain component. This is in centideg and is already a full width at half maximum so the strain is

$$S = \frac{\pi}{18000}(Y - Y_i)\ 100\%$$

As in the case of TOF data the parallel and perpendicular anisotropic strain components can be calculated by

$$S_\parallel = \frac{\pi}{18000}(Y + Y_e - Y_i)100\%$$

$$S_\perp = \frac{\pi}{18000}(Y - Y_i)100\%$$

Particle size broadening

For the case of a CW experiment the particle size broadening can be obtained from

$$\Delta d/d^2 = \frac{\Delta 2\Theta\cot\Theta}{d} = \text{constant}$$

From Bragg's law then

$$\Delta d/d^2 = \frac{2\Delta 2\Theta\cot\Theta\sin\Theta}{\lambda}$$

The broadening is

$$\Delta 2\Theta = \frac{\lambda\Delta d/d}{2\cos\Theta}$$

The first term in the expression for the Lorentzian broadening is of this form where

$$X = \frac{\Delta d}{d^2}$$

The particle size can be obtained by rearrangement of this expression and converting from centideg to radians by

$$p = \frac{18000K\lambda}{\pi X}$$

where K is the Scherrer constant. The units are Å. The anisotropic particle size components are given by

$$p_{\|} = \frac{18000K\lambda}{\pi(X + X_e)}$$

$$p_{\perp} = \frac{18000K\lambda}{\pi X}$$

In a similar way to the TOF functions #2 and #3, the average stacking fault separation can be obtained from the coefficient X_s by

$$p_s = \frac{18000\lambda}{\pi X_s}$$

The corresponding term in the Gaussian expression is the fourth one. Converting from centideg to radians gives the expression

$$p = \frac{18000K\lambda}{\pi\sqrt{8 \ln 2P}}$$

and again the units are Å.

Reflection Peak Widths

The reflection peaks are considered to have a definite cutoff at the wings where the magnitude of the function falls below some value. The cutoff positions depend on the nature of the profile function and its coefficients; they are found using numerical techniques by subroutine **PROWDT**; editing of the cutoff factors is done by **EDTPRF**. When a new function is installed, the subroutine **PRCALC** must be modified to call the new routine that generates the function and its derivatives.

Least Squares Theory

The refinement technique used by **GSAS** is the method of least squares and is performed by the program **GENLES**. In general the expressions for the calculated values corresponding to the set of crystallographic observations are transcendental and thus the least squares minimization function is nonlinear and the process is iterative.

For single crystal data the function usually minimized in **GSAS** is

$$M = \sum w(F_o^2 - SF_c^2)^2$$

where S is the scale factor for that data set (or histogram) and the sum is over the entire reflection set. The observed structure factors, F_o^2, are obtained by correction of the raw intensity scans for Lorentz-polarization effects and absorption in the **GSAS** routines **SCABS** and **SCMERGE** as well as background subtraction. The weights, w, are derived from an error propagation scheme during this process and are assumed to be uncorrelated. As indicators of the quality of the refinement a set of residuals are defined as

$$R = \frac{\sum|F_o^2-SF_c^2|}{\sum|F_o^2|}$$

and

$$R_w = \sqrt{\frac{M}{\sum w|F_o^2|}}$$

The reduced χ^2 or "goodness of fit" is defined by the minimization function as

$$\chi^2 = \frac{M}{(N_{obs}-N_{var})}$$

Alternatively and perhaps better, the function

$$M = \sum w(F_o-SF_c)^2$$

can be minimized. In this case the residuals become

$$R = \frac{\Sigma|F_o-SF_c|}{\Sigma|F_o|}$$

and

$$R_w = \sqrt{\frac{M}{\Sigma w|F_o|}}$$

The χ^2 is defined as above.

In analogy to the single crystal case, the least squares program **GENLES** minimizes for powder data the function (Rietveld, J. Appl. Cryst. 2, 65-71, 1969)

$$M = \sum w(I_o-I_c)^2$$

The quality of least squares refinement in this case is also indicated by some residual functions. These cover different parts of the pattern; one is for just that part of the pattern used in the refinement (marked "FITTED") and the other covers the entire pattern except excluded regions (marked "ALL"). Normally the entire pattern is included in the calculation so these values are the same. Optionally, the regions which have no contribution from Bragg peaks can be excluded from the first calculation. In analogy to the single crystal case, the residuals are defined as:

$$R_p = \frac{\Sigma|I_o - I_c|}{\Sigma I_o}$$

and

$$R_{wp} = \sqrt{\frac{M}{\sum w I_o^2}}$$

The reduced χ^2 is also defined the same way as in the single crystal case by

$$\chi^2 = \frac{M}{N_{obs} - N_{var}}$$

One can hand calculate an "expected R_{wp}" from

$$\text{expected } R_{wp} = \frac{R_{wp}}{\sqrt{\chi^2}}$$

A statistical measure of the serial correlation in the powder pattern differences ($\Delta = I_o - I_c$) as given by Durbin and Watson (Biometrica 58,1, 1971; Hill and Flack, J. Appl. Cryst. 20, 356-361, 1987) is also calculated from

$$D_{dw} = \frac{\sum_{i=2}^{N} (\Delta_i/\sigma_i - \Delta_{i-1}/\sigma_{i-1})^2}{\sum_{i=1}^{N} (\Delta_i/\sigma_i)^2}$$

If no serial correlation is present in the differences then D_{dw} is close to 2. The value at the beginning of a refinement is usually very close to zero because of the strong correlations and it increases to some maximum value as the refinement improves. Normally the correlations are such that a string of differences tend to have the same sign so that D_{dw} will be less than 2 in the final refinement. This indicates that some aspect of the profile model is inadequate and a systematic error remains in the analysis. Depending on the nature of the systematic error, the deviations of the refined parameters from the "true" values may be more is than indicated by the estimated standard deviations given by **GENLES**. Experience has shown that the principal systematic errors in most Rietveld refinements are in the profile functions and that they have little effect on the structural parameters resulting from the least squares analysis.

In **GSAS** it is also possible to provide as a set of observations the expected values for a set of interatomic distances assigning to each an appropriate standard deviation. These so called "soft constraints" are then used to generate a minimization function

$$M = K\sum w(d_o^2 - d_c^2)^2$$

The scaling factor K is used to adjust the contribution of these observations to the total minimization function. Usually K is set large in the beginning of a refinement and progressively made smaller as the model improves. This procedure is used to avoid an inadvertent bias in the results because of an incorrect preconceived notion about the value of the interatomic distances. The large contribution in the beginning of the analysis is used to avoid diverging refinements. These calculations are done in **GENLES** by **BNDCALC** and the editing is by routine **EDTSOFT**.

To minimize M by least squares, a set of derivatives of the function (F_c^2, I_c or d_c^2) with respect to a set of variables is obtained for each data point. These variables comprise a reduced set of parameters (atomic coordinates, thermal parameters, scales, powder parameters, etc.) obtained by successive application of three rectangular constraint matrices.

$$\frac{\partial F}{\partial v_i} = R_{il}U_{lk}S_{kj}\frac{\partial F}{\partial p_j}$$

These matrices are obtained from the rigid body constraints (R_{il}), the user constraints (U_{lk}) and the symmetry constraints (S_{kj}). The symmetry constraints are those required by the crystallographic point group for each atom position and affect the coordinates and anisotropic thermal parameters. The user constraints are those imposed on otherwise unrelated parameters because of some known or presumed relationship. The rigid body constraints are derived from a geometric description of molecular units where the least squares variables are distances, molecular origin coordinates and orientation angles.

This vector of derivatives is then used to produce the least squares normal equations which in matrix form are

$$\sum_{h=1}^{N_s} w_h(F^2_{ho} - SF^2_{hc})\frac{\partial F_{hc}}{\partial v_i} + \sum_{k=1}^{N_p} w_k(I_{ko} - I_{kc})\frac{\partial I_{kc}}{\partial v_i} + \sum_{i=1}^{N_d} w_i(d^2_{io} - d^2_{ic})\frac{\partial d_{ic}}{\partial v_i} = 0$$

where the sums are over the three types of observations. After expansion as a Taylor series and ignoring the high order terms, the set of observational equations becomes

$$\mathbf{Ax} = \mathbf{y}$$

where in the case of single crystal data

$$y_i = \sum_{h=1}^{N} w_h \Delta F^2_h \frac{|\partial F^2_{ch}|}{\partial v_i}$$

$$x_i = \Delta v_i$$

$$a_{ij} = \sum_{h=1}^{N} w_h \frac{\Delta|SF^2{}_{ch}|}{\Delta v_i} \frac{\Delta|SF^2{}_{ch}|}{\Delta v_j}$$

There are similar expressions for powder profile intensities and soft constraints on bond lengths. These equations are linear in the Δv_i and can be solved by inverting the symmetric matrix **A** by

$$\mathbf{A^{-1}Ax = A^{-1}y}$$

$$\mathbf{x = A^{-1}y = By}$$

This gives the set of shifts to be applied to the variables. They must be retransformed by the constraint matrices to give the set of shifts to be applied to the parameters

$$\Delta p_j = \Delta v_i R_{il} U_{lk} S_{kj}$$

In **GENLES** the matrix **A** is normalized before inversion by dividing each element by the square root of the product of corresponding row and column diagonal elements.

$$A'_{ij} = \frac{A_{ij}}{\sqrt{A_{ii}A_{jj}}}$$

The same is also done to the vector **y**

$$y'_i = \frac{y_i}{\sqrt{A_{ii}}}$$

This eliminates much of the difficulty of inverting a matrix with as much as 16 orders of magnitude range in the element values and gives a more robust refinement. The inverse matrix **B** and shift vector **x** are recovered by a similar transformation

$$B_{ij} = \frac{B'_{ij}}{\sqrt{A_{ii}A_{jj}}}$$

$$x_i = \frac{x'_i}{\sqrt{A_{ii}}}$$

The inverse matrix B is then used to obtain the variance-covariance matrix by normalizing by the reduced χ^2 .

$$\sigma^2{}_{ij} = \frac{B_{ij}}{\chi^2}$$

The square roots of the diagonal elements of this matrix are then the estimated standard deviations in the shifts that are applied to the least squares variables. It is then assumed that these esd's apply to the variables themselves and proper error propagation through the constraint matrices is used to obtain the esd's for the set of parameters.

These calculations in **GENLES** are performed by **MATSLV** and a set of subroutines called by it for matrix normalization (**MATSCL**), inversion (**LSSS** and **MATINV**) and renormalization (**MATUSCL**).

File Structures in GSAS

Introduction

In this section of the **GSAS TECHNICAL MANUAL** we describe the structures of each type of file generated by the system.

File Name Conventions

All files generated by **GSAS** in the course of calculations on a given structural problem have the same main file name; they differ only in the extension. This file name is chosen by the user with the **'EXPNAM'** option of the main **GSAS** command procedure. This name must be given by the user before beginning work on that problem with **GSAS**. All files are generated in the same directory as the first one and must always reside in a single directory.

EXPNAM.EXP - The Experiment File

Usually the first file produced by the system is the main data and control file, EXPNAM.EXP. On VMS systems, this file is a formatted ISAM (Indexed Sequential Access Method) file. Each record in this ISAM file is 80 characters or less long and starts with a 12 character key which is used by the system to fetch that record from the file; the information on that record is read in fixed format. For the UNIX versions of GSAS, the ISAM structure is simulated by routines within GSAS; the file itself is in direct access format. What follows is an essentially complete listing of all currently defined records in this file with an explanation of each, its format and the source of that record. The records are in alphabetical order by key (blank, upper case and numbers; no lower case or special characters are used for these keys by **GSAS**).

Overall data records

The initial section of records covers overall data for the entire experiment.

```
('      DESCR ',2X,A66)DESCR
```

Main descriptive title for the experiment (66 characters maximum). Entered into the file by **NEWEXP** immediately after creation by **OPNEXP** and edited by **EDTTITL**.

```
('     VERSION',I5)IVERSN
```

Version number for **GSAS**. This is the main flag used to determine whether any of the records in the experiment file have to be modified because of changes in **GSAS**. If the value of IVERSN on the record does not match the current version number then the subroutine **UPDATE1** is called to make the necessary changes. This check is done in subroutine **OPNEXP**, and is done by all programs in **GSAS** that open this file with READ/WRITE access.

```
('    HSTRYnnn',1X,67A)TEXT
          nnn=version number for experiment file
```

History record for **GSAS**; a new one is written as each version of the experiment file is produced and by programs that modify the contents of the file. The TEXT includes the name of the **GSAS** program that produced the file, its version number, and the date and time the file was accessed by that program. Usually listed is some brief indication of what was done by that program; for example, **EXPEDT** lists the major menu requests and **GENLES** gives an indication of the refinement progress. Programs that only read information from the experiment file do not produce a new version or write history records.

```
('  DSGL CDATc',2X,A)CDATA
            c = 1 to 9(max)
```

Distance and angle program controls. The controls are written as a free format string. They are defined and modified by **EDTDIST**. There is one of these cards for each phase, 'c'. The data are flags controlling distance and angle calculation limits and inclusion of data from a peak search of Fourier maps.

```
('  FNDP CDATc',2I5) NPEAKS,MININT
('  FNDP HDATc',15A4) (LHST(I),I=1,M)
           c = 1 to 9(max)
```

Control data for **FINDPK**, the peak search routine for data from the SCD instrument at LANSCE. The first record gives the maximum number of peaks to accept from a histogram and the minimum peak value to use. The second gives the list of histograms to be searched. The first item in the list can be either of the strings, "REST" or "ALL", or a number.

```
('  FOUR CDATc',2X,2A5,A2,A5,A8)(FDATA(I),I=1,5)
            c = 1 to 9(max)
```

Fourier map controls; each control is read as a character string and indicates the type of map, section direction, phase number, print control and a special d_{min} if such is needed. One of these records is written by **EDTFOUR** for each type of map to be calculated. Fourier map control data for only one phase can be generated at a time. They are read by **FOURIER** to set up map calculations.

```
('  GNLS  RUN ',A43,I4,G17.5)TEXT,NCYCLES,CHISQ
```

Least squares run indicator; it gives the date, time and total number of cycles attempted for the experiment and the latest value of χ^2. This is used by **POWPLOT** to produce the secondary plot title and by **DISAGL** to coordinate the variance-covariance matrix with the structural parameters.

```
('  GNLS CDATc',2X,8A8)(CDATA(I),I=1,M)
            c = 1 to 9(max)
```

Least squares controls (maximum number of cycles, etc.). Each control is an 8 character string and is entered by **EDTLSQ**. There may be more than one of these records. The controls are read for **GENLES** by **RDLSCNTL**.

The next few records contain the control data for **INTEGRATE**, the program for extracting intensity data from the LANSCE single crystal instrument, SCD. They are edited by **EDTINGRT**. They are read in the integration program by **INGREAD**.

```
('  INGT CDAT1',2F5.3,F6.3)WNDOX,WNDOZ,EMIN
```

These parameters define the *x*,*y* dimensions of the reflections for integration. The first two values define the spot size and the region to used for background evaluation. The last item, EMIN, is used for a minimum count cutoff to limit the region of integration.

```
('  INGT CDAT2',2F6.1,12X,2F6.3)SG0,SG1,BE0,BE1
```

These data define the shape of the peak along the time direction. They are quite similar to those used in the powder profile parameters.

```
('  INGT CDAT3',2F5.2,7F4.1,F6.3,1X,A,2I3)BINMIN,VRATMX,(RAT(I),I=1,7),
                                            DMIN,SOLLER,IXL,IXU
```

Integration limiting and final data selection flags. BINMIN defines the minimum fraction of a peak included in the integration for accepting the value. VRATMX determines the maximum ratio peak to background allowable for the peak to be included. This can get very large if the peaks are very dense. The seven RAT values are I/sig(I) cutoffs used for creating a table of data with which the quality of the data can be evaluated. SOLLER and IXL and IXU define the Soller shield used on SCD from 1982 until mid 1988.

```
('  INGT HDATc',15A4) (LHST(I),I=1,M)
            c = 1 to 9(max)
```

The list of histograms for integration. Histograms can be summed together before integration of the reflection data. This is accomplished by entering -h for histograms which are to be added to the current data before integrating.

```
(' AFAC aaaa  ',9F7.0)(FFAC(I),I=1,9)
           a = element symbol
```

The first atom data record for atom type 'a'. The element symbol consists of the standard two letter chemical symbol (upper case) and the valence as a sign and a numerical value, e.g. 'TI+4'; this is part of the key. The 9 values are the coefficients for the x-ray scattering factor for that chemical species as listed by Cromer & Waber (1974), International Tables for X-ray Crystallography, Vol. IV, p 99-101. This and the succeeding 'AFAC' cards are copied from the atom data file by **REDSCTF** whenever a new atom TYPE is input by the user into **EXPEDT**. These records are read by **RDSCFT** in **GENLES**.

```
(' AFAC aaaa M',9F7.0)(MFFAC(I),I=1,9)
           a = element symbol
```

This record is the exception to the rule just noted. It is present only when a magnetic form factor has been entered into the experiment in **EXPEDT** using the form factor editing option in the 'Least Squares' editing menu and magnetic form factors are selected. The data for this record is not currently in the atom data file to be described later. Data in table 4.4.5.1 of International Tables for X-ray Crystallography, Vol. C, can be used as listed for the elements and ions in that table. Data for other atoms or ions can be derived from tables

4.4.5.2-14 of that source. Alternatively, one can read a file containing the scattering factor data as a function of sinθ/λ and fit it to the needed function in subroutine **EDTMFF**.

```
(' AFAC aa_nnn',F7.0,4F6.0)WT,BLEN,RNMU,RNMUX
```

The isotopic data for 'aa_nnn' where 'aa' is the chemical symbol (upper case) and 'nnn' is the isotope. The data are isotopic weight, real neutron scattering length, and the wavelength dependent and wavelength independent neutron absorption cross sections. Since there are only a very few atomic isotopes for which an imaginary scattering length is needed, we do not currently have that data in our data base. If 'nnn' is blank then the data are for the natural abundance element. Synthetic elements do not have 'natural abundance' data.

```
(' AFAC aa_SIZ',2F10.2,F5.2,I5)DRAD,ARAD,PRAD,COLOR
```

This record contains default atom size data for distance/angle calculations and for the structure plotting programs.

```
(' AFAC aa_XAB',1X,5F6.0)(RXMU(I),I=1,5)
```

The x-ray absorption cross sections for Cr, Fe, Cu, Mo and Ag Kα radiation.

```
(' AFAC aa_XAN',1X,10F6.0)(XFP(I),XFPP(I),I=1,5)
```

The real and imaginary parts of the anomalous dispersion for Cr, Fe, Cu, Mo and Ag radiation for the a-th atom type.

```
(' EXPR  HTYPc',2X,12(A4,1X))(HTYP(I),I=1,NHST)
             c = 1 to 9(max)
```

The histogram type flags, HTYP, are 4 character strings which indicate the type of sample (P: powder or S: single crystal), type of radiation (N: neutron or X: x-rays), type of data (T: time of flight or C: constant wavelength) and the status of the data set (blank: use in least squares, D: dummy powder histogram not processed by **GENLES**, F: SCD histogram peak positions have been determined by **FINDPK**, G: SCD histogram peak positions found by **FINDPK** but will not be used, I: SCD histogram intensity data generated by **INTEGRATE**, N: new SCD histogram not yet processed by **FINDPK**, R: read powder histogram, X: powder profile not processed by **POWPREF** or *: do not use in least squares). Thus the flag 'PNT ' means that this histogram is neutron TOF powder data that can be used in a least squares refinement. The special histogram type 'RSN' is used for "soft" constraints which are treated as a set of observations and are placed in their own histogram. There is one type for each histogram and they are in the order of the histogram numbers. These flags are generated in several places in **GSAS**, and the records are written by **WRHTYP** and read by **RDHTYP**.

```
(' EXPR  NATYP',I5)NATYP
```

The number of atom types. The maximum number of atom types is 9 due to limitations imposed by array sizes in **GENLES** and **EXPEDT**. This value is updated by **TYPINS** and **TYPDEL**. This value is read by **RDSCFT** in preparation for reading the scattering factors.

```
(' EXPR  NHST ',I5)NHST
```

The number of histograms, **NHST**, loaded into the **GSAS** system for this problem. This value never decreases and is updated when new histograms are read by **HSTINS** for powder data, **REDHST** for SCD single crystal data, **CAD4RD** for Enraf-Nonius CAD4 data and generated by **EDTSOFT** for soft constraint data.

```
(' EXPR ATYPnn',2X,A8,I5,2F10.0,F5.2,I5)TYPE,NATOM,DRAD,ARAD,PRAD,COLOR
             n = 1,NATYP
```

Record contains the atom type, the number of atoms of that type in all phases and atom radii limits for distance and angle calculations and data for structure plotting. The type matches that used for an individual atom entry (see below) and is composed of the chemical symbol (upper case) valence (if any) and isotope (if any). The form of the type is 'aasv_nnn' where 'aa' is the chemical symbol, 's' is the valence sign (+ or -), 'v' is the valence (typically 1-6) and 'nnn' is the isotope number. The number of atoms is incremented when a new atom of that type is added and decremented when an atom is deleted. If this value reaches zero then this record is deleted, however the 'AFAC' records for this atom type are not deleted. The atom radii are edited by **EDTDIST** and read by **DISAGL**.

```
(' EXPR ftypRL',I10) LENREC
```

This record is written by **FOURPRT4** within **FOURIER** and contains the length of records in the 'ftyp' Fourier map file. 'ftyp' is one of 'FOBS', 'FCAL', DELF', PTSN', or 'DPTN'. It is read by the Fourier map processing or plotting routines in preparation for opening the appropriate map file.

```
(' EXPR NMXTLS',9I5)(NMXTLS(IPHAS),IPHAS=1,9)
```

This record is written by **INDEXSCD** and records the number of separate crystals found for each phase in a single crystal experiment. These crystals may be multiple crystals in a histogram, or they may be separate settings of a single crystal which fell off in the middle of an experiment, or separate crystals used because of crystal loss, etc. The code allows for up to nine crystals per phase. The record is read in several places in the processing of single crystal data from the SCD instrument.

```
(' EXPR NPHAS ',9I5)(NPHAS(IPHAS),IPHAS=1,9)
```

Phase flags for phase number IPHAS. The value of each flag is 1 if there is just nuclear phase information, 2 for mixed nuclear and magnetic phase information, 3 for magnetic only phase information, or zero if the phase is absent. This record is updated by **EDTPHAS** and is read in many places in **GSAS**.

Crystal structure records

The next section of records are specific structural information for each phase, p, in the sample.

```
('CRSp    PNAM',2X,A66)PNAM
```

A characteristic name for the phase; entered by the user in **EDTPHAS** and used for various heading titles.

```
('CRSp   ABSCO',7F10.2)(XAB(I),I=1,5),RNMU,RNMUX
```

Computed absorption coefficients for this phase based on the chemical formula and the five x-ray wavelengths and the two neutron absorption coefficients. This and the next three records are changed by **EDTCOMP** any time the chemical formula is changed.

```
('CRSp   ATYPS',I5)NATYPS
```

Number of atom types for this phase; used to read the formula record, `'CRSp   FRMLc'`, shown below.

```
('CRSp   F000 ',2F10.0)FNEUT,FXRAY
```

The F_{000} scattering factors for neutrons and x-rays based on the chemical formula.

```
('CRSp   FRMLc',4(2X,A8,F6.2)(ATYP(I),NAT(I),I=1,NATYPS)
             c = 1 to 1+(NATYPS-1)/4
```

The contents of the unit cell for this phase. Used to calculate absorption coefficients, formula weight, density and F_{000} values.

```
('CRSp   NATOM',I5)NATOM
```

The number of atom positions for this phase. This record is updated by **ATMINS** and **ATMDEL**; if it reaches zero the phase can be deleted by **PHASDEL**.

```
('CRSp  ABC   ',3F10.6,4X,A1,4X,I1)(ABC(I),I=1,3),IREF,IDAMP
('CRSp  ABCSIG',3F10.6)ABCSIG(I),I=1,3
('CRSp  ANGLES',3F10.4)ANGLES(I),I=1,3
('CRSp  ANGSIG',3F10.4)ANGSIG(I),I=1,3
```

The first record contains the real lattice edge lengths for the phase, a refinement flag and a damping factor. The third contains the lattice angles. If the refinement flag is 'Y' then the lattice parameters (as reciprocal metric tensor elements) will be refined. Refinement is possible with powder diffraction data and single crystal data from SCD type instruments. The damping defines what fraction of the calculated shift is applied to give the new values of the parameters. The applied shift is (10-IDAMP)/10 times the calculated shift. The second and last records are the estimated standard deviations in the lattice parameters.

```
('CRSp  ATmmmA',2X,A8,4F10.6,A8,I4,1X,3A1) ATYP,X,Y,Z,FRAC,
                         NAME,MULT,(IDAMP(I),I=1,3)
('CRSp  ATmmmB',6F10.6,2X,4A1) (UIJ(I),I=1,6),(CODE(I),I=1,4)
      m = 1 to NATOM
```

Atom parameter records for atom 'm'; the first one contains the atom type (matches one of the atom types given above), fractional coordinates, atom fraction, atom name (chosen by user), multiplicity of atom site, damping factors for FRAC, XYZ and UIJ. The second contains the temperature factors; if CODE(1) = 'I' then UIJ(1) is U_{iso}, if CODE(1) = 'A' then six anisotropic u_{ij} values are given. If CODE(2) = 'F' then FRAC is to be refined; if CODE(3) = 'X' then XYZ's are to be refined as permitted by symmetry; and if CODE(4) = 'U' then U_{iso} or the u_{ij}'s are to be refined as permitted by symmetry. These records are written by **WRTATM** and read by **REDATM**; the parameters are edited by several atom editing routines called from **EDTATM**.

```
('CRSp  ATmmmM',3F10.5,2(1X,A2),3F10.3) (ATMON(I),I=1,3),
                        CODE(5),IDAMP(4),(ATMON(I),I=4,6)
      m = 1 to NATOM
```

The magnetic moment data record for atom 'm', ATMON(1-3) give the components of the magnetic moment along the three orthogonal directions defined earlier, ATMON(4-6) are the magnitude of the moment and the moment orientation angles, ψ and ω relative to the orthogonal Z- and X-axes. CODE(5) = 'M' to refine the moment and IDAMP(4) is the damping factor to be applied as defined above.

```
('CRSp  CELVOL',2F10.3)CELVOL,SIGCVL
```

The unit cell volume and esd; this record is updated each time the lattice parameters are changed.

```
('CRSp  DENSTY',F10.3)DENSTY
```

The density of this phase in Mg/m^3; this record is updated by **EDTCOMP** any time the chemical formula is changed. It is not affected by atom parameter refinement or atom editing.

```
('CRSp  FMHSTn',20I3)HSTLST
             n = 1 to 9 (max)
```

The list of included histogram numbers to use for the Fourier calculation. The structure factors are read from the histograms in the order as shown. The last occurrence of a structure factor is the one used in the calculation. Mixing of x-ray and neutron histograms is not allowed. This record is written by **EDTFOUR** and read by **FOURIER** when the map is calculated.

```
('CRSp  FMPCTL',9I5)NXI,NYI,NZI,NXO,NYO,NZO,NXT,NYT,NZT
```

This record gives the number of steps along the cell edges, the starting step position and the ending step position for a Fourier map calculation. It is written by **EDTFOUR** and read by **FOURIER** when the map is calculated. This information is then written in the second record of the Fourier map file during processing by **FOURIER** (see below).

```
('CRSp  FPK   ',2X,A66)TEXT
```

This record gives the time and date of extraction of peak positions from a Fourier map along with the map type that was processed by **FORSRH**. It is written by **FRSHR**.

```
('CRSp  FPKnnn',3F10.5,F10.3)(XN(I),I=1,3),IXN
```

These records contain the positions and heights of the peaks extracted from a Fourier map. They are written by **FRSHR** and can be read by **DSGREAD** for distance and angle calculations by **DISAGL** and **FPLTATM** for plotting on contoured maps produced by **FORPLOT**

```
('CRSp  MRG-R ',4(A,F6.3),A,I5)' wR(Fsq)=',R1,' wR(F)=',R2,
                         ' R(Fsq)=',R3,' R(F)=',R4,' N(I)=',NREF
```

Record written by **SCMERGE** giving the R-factors from the merge of equivalent reflections and the number of resulting unique reflections.

```
('CRSp  MXDSTR',F10.5) DSTRMX
```

The maximum d^* for magnetic reflections in this phase. This record is produced by **ATMMAG** and used by **CELLINP**.

```
('CRSp  PEAKRD',2F6.0,11F5.2)PKMAX,PKMIN,FDRAD,FARAD,
                               (REJRAD(I),I=1,NATYP+1)
```

Distance and angle code controls for processing peak information from **FORSRH**. The data are peak minimum and maximum values, the radius of the peak for distances and angles, and the peak overlap rejection radius for each atom type and for the peaks themselves. This record is produced by **EDTDIST**.

```
('CRSp  SG SYM',2X,A20)SPSGSYM
```

The space group symbol for this phase. The symbol is entered by the user to **SPSGSYM** which calls the space group interpreting routine **SGROUP** before entering it into the file. This record is read in other parts of **GSAS** which then call **SGROUP** to produce all the relevant symmetry information.

```
('CRSp  SPAXIS',3F5.0,4x,A,6F5.0)PAXIS,NAXIS,UAXIS,VAXIS
```

The principal broadening axis, PAXIS, for this phase; it is used to calculate the anisotropic broadening terms in some of the powder profile functions. If NAXIS is 'Y' then two additional axes are defined for the sublattice of reflections that are subject to a different anisotropic particle size broadening than the nonsublattice reflections. This facility is used by some of the profile functions to simulate broadening due to stacking faults. This record is edited by **EDTPRF**, and input by **PRFCINP** and output by **PRFCOUT**.

```
('CRSp  SPNFLP',12F4.0)(SPNFLP(I),I=1,12)
```

This record contains the current state of the spin flip operations to create the magnetic space group from the nuclear one for this phase. The values are +1.0 for no spin flip and -1.0 for spin flip. This record is created by **ATMMAG** and read by **POWPREF** and **ATMSINP**.

```
('CRSp  UCRFLn',20I3)(IPARM(I),I=1,60)
             n=1,3
```

Refinement flags used in **CELLLSQ**. This record will only appear while processing LANSCE SCD data.

```
('CRSpe EXTSN ',I5,2X,3A,2X,3I1)EXTTYP,IEXCOD,(IDAMP(I),I=1,3)
('CRSpe EXTSN1',3E10.3)(EXTSING(I),I=1,2),EXTRPRI
```

Single crystal extinction flags and coefficients. They are edited by **EDTEXTS**, input by **EXTSINP** and output by **EXTSOUT**. There is a set for each phase and crystal element in the sample.

```
('CRSpe HKLDnn',4F10.4)
```

These records describe the crystal shape for use in absorption calculations in **SCABS**. They are written and edited by **EDTPLNS**.

```
('CRSpe O-CHI ',2F10.3) CHI,SIGCHI
('CRSpe O-OMG ',2F10.3) OMG,SIGOMG
('CRSpe O-PHI ',2F10.3) PHI,SIGPHI
```

Single crystal element orientation angles. The three orientation angles required to position the 100 reciprocal lattice vector into the reflecting position with the *hk0* set of vectors in the standard xy plane on a single crystal goniometer. The ω angle is measured away from the y-axis, χ from the negative z-axis and ϕ is arbitrary. These records are initially written by **INDEXSCD** and later are modified by **CELLLSQ** which adds the sigmas.

```
('CRSpe PTYPE ',2X,A8,I4,F8.2)PTYPE,NPLANES,PHI0
```

The record describes the way that the faces of a faceted crystal are defined. The data are PTYPE, a flag defining the face definition, NPLANES, the number of faces, and PHI0, the ϕ angle at which the diffractometer *x*-axis and the crystal *x*-axis are coincident if PTYPE='3 POINTS' and θ,χ and ω are zero. This record is written by **EDTPLNS** and is read by **PLANIN** in the single crystal absorption program **SCABS**.

```
('CRSpe XD0   ',3F10.2) (XD0(I),I=1,3)
('CRSpe XD0SIG',3F10.2) (SIGXD0(i),I=1,3)
```

Crystal miss-centering vector and its estimated standard deviation. These records are initially written by **INDEXSCD** and modified by **CELLLSQ**. This data is used by all codes which need to calculate detector coordinates for reflections from reflection indices or to calculate reflection indices from detector locations.

Histogram/phase records

The next section of records contains information that depends on both the histogram, h, and crystalline phase, p; hence the key prefix 'HAP'.

```
('HAPphh ZONE',4I5)ZONE
```

The first three coefficients describe the zone axis restricting the reflection set for a powder pattern. The fourth coefficient is the layer number. If all zeros there is no restriction on the reflection set. This record is written by **EDTZONE** and read by **REFGEN** in **POWPREF**.

```
('HAPphhELMFRn',G16.4,4X,A,I5)SCALE,REFCOD,DAMP
```

Crystal element fraction for this phase and histogram combination, refinement flag and damping flag. This is used for a single crystal histogram. Editing is done by **EDTSCAL**, least squares input by **SCALINP** and output by **SCALOUT**.

```
('HAPphhEXTMAX',A,F8.5)TEXT,EXTMAX
```

This record gives the maximum extinction correction applied to any reflection in this phase and histogram. It is written by **SNGLXTL** in **GENLES** as each histogram is processed.

```
('HAPphhEXTPOW',E15.6,4X,A1,4X,I1)EXTPOW,IREF,IDAMP
```

The powder extinction coefficient, its refinement flag and damping factor. These are edited by **EDTEXTP**, input by **EXTPINP** and output by **EXTPOUT**.

```
('HAPphhNAXIS ',I5)NAXIS
```

This gives the number of preferred orientation axes in the March-Dollase model used for powder diffraction data. It determines the number of `'HAPphhPREFOn'` (see below) records are read for this phase/histogram combination. It is created by **EDTPRFO** and used by **PRFOINP**.

```
('HAPphhPHSFR ',G15.6,4X,A1,4X,I1)SCALE,IREF,IDAMP
```

Phase fraction for this phase and histogram combination, refinement flag and damping flag. This is used for a powder diffraction histogram. Editing is done by **EDTSCAL**, least squares input by **SCALINP** and output by **SCALOUT**.

```
('HAPphhPRCF  ',2I5,F10.5,4X,I1,20A1)
                  PTYP,NCOF,CTOF,IDAMP,(IREF(I),I=1,NCOF)
('HAPphhPRCF c',4E15.6)(COF(I),I=1,NCOF)
             c = 1 to 1+(NCOF-1)/4
```

The first record contains the powder profile type, number of coefficients, cutoff factor, damping flag and a refinement flag for each coefficient. The second and subsequent record (c = 1,...) contain the coefficients with four per record. These are edited by **EDTPRF** and routines called by it, input by **PRFCINP** and output by **PRFCOUT**.

```
('HAPphhPREFOn',4F10.5,4X,A1,2I5)PRFCOF,(PHKL(I),I=1,3),REFCOD,DAMP,TYPE
             n=1,NAXIS
```

This record gives the preferred orientation coefficient, direction, refinement code, damping factor for preferred orientation axis 'n', and preferred orientation function type. The number of these records is determined from the `'HAPphhNAXIS '` (see above). These are edited by **EDTPRFO**, input by **PRFOINP** and output by **PRFOOUT**.

```
('HAPphhXTLELM',2X,9I2) (XTLELM(IPHAS,IELEM)
```

This record notes which crystal elements of phase, IPHAS, are present in this histogram. The record is written by **INDEXSCD** and read by all programs needing to process reflection data, such as **INDEXSCD**, **CELLLSQ**, and **INTEGRATE**. A dummy record with XTLELM(1,1)=1 is entered for powder histograms.

Histogram records

The next section of records contains only histogram specific information. This section is described in four parts each covering the records that are specific to particular types of histograms

All diffraction histogram types

The following records are found in the experiment file for all diffraction histogram types. Some of these are not needed for histograms from TOF neutron single crystal diffractometers (SCD instruments); they will be so indicated

```
('HST hh  HFIL',2X,A66)RAWNAM
```

The file name of the **GSAS** standard powder data file or SCD raw data file which is the source of this histogram. This name uses whatever logical names the user had in force to describe this file at the time the file was introduced to experiment by**EXPEDT** for powder data, by **REDHST** for SCD data, or by **CAD4RD** for single crystal x-ray data.

```
('HST hh  HNAM',2X,A66)HNAM
```

A histogram title taken from the title record on the **GSAS** standard powder data file or from the cataloging string for SCD data.

```
('HST hh  IFIL',2X,A66)INSTNAM
```

The file name of the instrument parameter file associated with this histogram. This file name also uses logical names.

```
('HST hh IRAD ',I5)IRAD
```

This is an integer (1 to 5) indicating which characteristic radiation (Cr, Fe, Cu, Mo or Ag Kα, respectively) was used for the data collection. This record originates from the instrument parameter file and is read by **PDCALC** or **SNGLXTL** as the histogram is processed. It is only needed for x-ray data. If IRAD is zero the wavelength is not one of the five standard ones and special anomalous dispersion data is needed for the histogram; these are the FFANS records described below.

```
('HST hh NREF ',I5,F10.4,4X,A1)NREF,DMIN,IFFOS
```

The number of reflections in the 'EXPNAM'.REFPhh or the 'EXPNAM'.REFShh reflection file, the minimum d-spacing and a flag for powder data indicating whether F_o^2's have been extracted from this histogram. This record is produced when the reflections are generated by **REFGEN** for powder data and by the several routines that process single crystal data. The flag is set by **PDCALC** to 'Y' after it has produced F_o^2's and places them in the reflection file.

```
('HST hhFFANSc',2X,A8,2F10.3,3X,2A1,I5)ATYP,DELFP,DELFPP,IRE,DAMP
             c = 1,NATYP
```

The special anomalous dispersion coefficients for x-ray data with a non-standard wavelength. Included is two refinement flags and a damping factor. These records are required when IRAD is zero and there must be one for each atom type in the same order as the `' EXPR ATYPnn'` records above. These are edited by **EDTFFAC**, input by **FFACINP** and output by **FFACOUT**.

```
('HST hhOMEGA ',F10.3)OMEGA
('HST hhCHI   ',F10.3)CHI
('HST hhPHI   ',F10.3)PHI
```

These are the sample orientation angles with respect to the diffractometer which are used for generalized texture analysis of polycrystalline samples. They are defined in much the same way as for a single crystal diffractometer (see `'CRSpe O-CHI '`, etc. records above). These records are wirtten by **HSTCHG**.

```
('HST hhREFLEN',I5)REFLEN
```

This record gives the length of the records in the .REFhht files, where 't' is 'M', 'P' or 'S' for single crystal merged data, powder or single crystal data respectively.

Powder histogram records

All of this information which is related to powder histograms is entered into the experiment file by **HSTINS** when the histogram is first read.

```
('HST hh BANK ',I5)IBANK
```

The counter bank number for the diffractometer.

```
('HST hh CHANS',6I10)HOLDOFF,ICLMP,NCHANS,CHEKHST,MCHANS,ISAMP
```

The holdoff for the first channel in the output powder histogram from **POWPREF** (HOLDOFF), the number of original data channels combined in each bin (ICLMP), number of steps in the original profile (NCHANS), a checksum for the intensities (CHEKHST), the number of bins used in the calculations (MCHANS), and the sampling frequency (ISAMP). The checksum is computed from the raw data and is used to check whether a data set has been read previously.

```
('HST hh DUMMY',I10,2X,A,3X,2F10.3)NCHAN,BINTYP,(BCOEF(I),I=1,4)
```

These are the control values needed for dummy powder histogram generation. NCHAN is the number of channels desired, BINTYP is either 'CONST' or 'LOG6' and BCOEF includes the holdoff for the first channel and either the step size or the clock increment.

```
('HST hh EPHAS',9I5) (EPHAS(I),I=1,9)
```

Flags to control the extraction of integrated intensities for the reflections in the histogram. The flags are generated in **EDTEXTFOS** and read in various places in **GENLES**.

```
('HST hh ICONR',3F10.0,2X,3A1,4X,I1,F10.0,I5,F10.0)
                  DIFC,DIFA,ZERO,IREF,IDAMP,POLA,IPOLA,KRATIO
('HST hh ICONS',3F10.0,2X,3A1,4X,I1,F10.0,I5,F10.0)
                  DIFC,DIFA,ZERO,IREF,IDAMP,POLA,IPOLA,KRATIO
```

These are the diffractometer constants for a powder diffractometer. In the case of a TOF diffractometer the constants relate d-spacing and TOF in μsec. For CW data the same record holds wavelength data, LAM1 and LAM2, in place of DIFC and DIFA and KRATIO is added to the record. The polarization coefficient POLA is absent for neutron data. The ICONR record contains the initial values for these coefficients as obtained from the instrument parameter file and is used to reset the values if needed. These are edited by **EDTDIF**, input by **DIFSINP** and output by **DIFSOUT**.

```
('HST hh MAXRF',I5)MAXRF
```

The maximum number of overlapping reflections for any point in the powder pattern. This value is determined by **HSTMACH** in **POWPREF** and is used to determine the size of the arrays that hold reflection information in **PDCALC**.

```
('HST hh NEXC ',I5)NEXC
```

The number of excluded regions in the pattern. There is always at least two; one for the short end of the pattern and one for the long end. These are edited by **EXCLCHG**. The first excluded region record for TOF data and the last one for CW data can be modified only by setting the minimum d-spacing in **ESTDMIN**.

```
('HST hh NFXB ',I5)NFXB
```

The number of fixed background points in this histogram.

```
('HST hh NPHAS',9I5)NPHAS
```

Phase flags for this histogram. The value of each flag is 1 if there is just nuclear phase information, 2 for mixed nuclear and magnetic phase information, 3 for magnetic only phase information, or zero if the phase is absent. This record is updated by **EDTHPHAS** and is read in many places in **GSAS**.

```
('HST hhABSCOR',2E15.6,4X,A1,2I5)ABSCOR(I),I=1,2,IREF,IDAMP,IABTYP
```

The powder absorption coefficients, refinement flag, damping flag, and absorption type flag. These are edited by **EDTABS** and input and output by **ABSCINP** and **ABSCOUT**, respectively.

```
('HST hhBAKGD ',2I5,4X,A1,I5,4X,A1)BTYP,NCOF,IREF,IDAMP,IFULL
('HST hhBAKGDc',4E15.6)(BCOF(I),I=1,NCOF)
             c = 1 to 1+(NCOF-1)/4
```

The first record contains the background function type, the number of coefficients (maximum of 36), refinement flag, damping factor and full background refinement flag. The second and subsequent records contain the coefficients. These are edited by **EDTBAK** and are input and output by **BACKINP** and **BACKOUT**, respectively.

```
('HST hhBNKNAM',A) BNKNAM
```

The name of the data bank used to collect the histogram. This name for TOF instruments usually gives the detector bank location. The record is purely for descriptive purposes.

```
('HST hhBNKPAR',5F10.0,2I5)DIST,TTHETA,TILT,SEPN,HGHT,NTUBE,ITUBE
```

This record describes a TOF detector bank. This data is used by **FSTBUSBIN** to compute the spectrum shift factors required to bin multiple detectors into a single data set when the `'HST hhBNKTCc'` records are absent. The second term, TTHETA (2Θ), is read as part of the preparation of powder plot titles and for powder absorption and extinction calculations. This record originated from the instrument parameter file.

```
('HST hhBNKTCc',8F8.2)(DIFC(I),I=1,NTUBE)
             c = 1 to 1+(NTUBE-1)/8
```

These are the individual DIFC values for each tube in a bank of detectors; these are used by **FSTBUSBIN** to calculate the spectrum shift factors. As with the previous record, these records are copied from the instrument parameters file.

```
('HST hhEXCeee',2F10.3)(EXCM(I),EXCX(I),I=1,NEXC)
             e = 1 to NEXC
```

The excluded regions from EXCM to EXCX in msec or degrees 2Θ; there are at least two of these records. These records are edited by **EXCLCHG** and **ESTDMIN**. The excluded regions are marked in the profile by **HSTPROC**.

```
('HST hhFXB cc',3F10.2)(TOFB(I),BAK(I),SBAK(I),I=1,NFXB)
             c = 1 to NFXB
```

The position, fixed background and estimated error in the fixed background value. If these are present they should include a point at each end of the histogram even if the values are zero at those points. These are edited by **FBAKCHG**.

```
('HST hhHSCALE',G15.6,4X,A1,4X,I1)SCALE,IREF,IDAMP
```

Scale factor for this histogram, refinement flag and damping flag. The net scale factor for a phase in a powder histogram in the product of this scale and the 'HAP' PHSFR listed above. This feature can be used in multiphase mixtures to separate the phase fraction from the histogram scale. Editing is done by **EDTHSCAL**, least squares input by **HSCALINP** and output by **HSCALOUT**.

The next series of five record types characterize the incident spectrum and are copied from the instrument parameter file. The data are defined by the program **FITSPEC**. All of these are read by **HSTPROC** the first time a powder histogram is processed by **POWPREF**.

```
('HST hhI HEAD',2X,A66)IHEAD
```

A title taken from the incident spectrum raw data file.

```
('HST hhI ITYP',I5,2F10.4,I10)ITYP,TMIN,TMAX,CHKSUM
```

The incident intensity function type, the minimum TOF, the maximum TOF over which the function can be applied and a checksum on the incident spectrum. The latter is used to check if this incident data has been applied to another histogram.

```
('HST hh TRNGE',2F10.5)TMIN,TMAX
```

The actual range of data in msec TOF or degrees 2Θ as delimited by the excluded regions. This record is written by **HSTPROC** and is used by **BACKCAL** and **CALCBAK** for computing function #1 (Chebyschev series).

```
('HST hhICOFFc',4E15.6)(VINC(I),I=1,12)
             c = 1 to 3
```

Coefficients for the incident intensity function; they are expressed in terms of TOF in milliseconds. If ITYP above is zero these records are not needed.

```
('HST hhIECOFc',4E15.6)(SINC(I),I=1,12)
             c = 1 to 3
```

The σ's for each of the coefficients. If ITYP above is zero these records are not needed.

```
('HST hhIECORc',10F6.3)(PINC(I),I=1,78)
             c = 1 to 8
```

The elements of the correlation matrix in upper triangular form for the incident intensity coefficients. These with the σ's are used to calculate the σ in the calculated incident intensity at each point in the profile. If ITYP above is zero these records are not needed.

```
('HST hhPRCFn ',2I5,F10.5,4X,I1,20A1)
                  PTYP,NCOF,CTOF,IDAMP,(IREF(I),I=1,NCOF)
            n = 1,NTYP
('HST hhPRCFnc',4E15.6)(COF(I),I=1,NCOF)
             c = 1 to 1+(NCOF-1)/4
```

These records give the NTYP sets of profile functions available for the histogram with their default coefficients. The first record contains the powder profile type, number of coefficients, cutoff factor, damping flag and a refinement flag for each coefficient. The second and subsequent records (c = 1,...) contain the coefficients with four per record. These records are obtained from the instrument parameter file and are copied to the 'HAP' records listed above to initialize the profile coefficients for the specific histogram/phase combination. If the user changes to a different type of profile function, these records are the source of the starting values. The first set defines the default profile function type for this histogram, i.e. PTYP for the first set does not have to be 1.

Single crystal histogram records

The following records appear when the histogram is from a single crystal diffractometer. Some are only needed for x-ray or CW neutron diffraction data. Any records that are specific to TOF instruments are described in the next section.

```
('HST hh  INST',I5)INSTNO
```

Record pointing to the appropriate instrument parameter records.

```
('HST hh CDAT1',2(2X,A),1X,L1,3F6.3)DATASRC,ABSTYPE,PRTREF,
                                      SHPRAD,ERRINS,DSMAX
```

Histogram dependent control data for **SCABS**. DATASRC is the radiation type (i.e. CuKa), ABSTYPE is the absorption correction type, PTREF is a logical controlling the printing of reflections by **SCABS**, SHPRAD is the sphere radius in mm, ERRINS is the instrument error constant and DSMAX is the maximum value of d*. Written by **EDTSCAB** and read by **SCABS**.

```
('HST hh NPSI ',4I5)NPSI,PSIHKL
```

The number of measurements of the ψ-scan reflection and its *hkl* index. This record is written by **PSISCNDTA** in **CAD4RD** and read by **EDTSCAB** and **SCABS** for absorption corrections.

```
('HST hh NREFM',I5,F10.4)NREFM,DMIN
```

Used only for single crystal data collected with constant wave-length methods. This gives the number of reflections in the merged data set generated by **SCMERGE**. The DMIN is carried over from the raw unmerged data set. This is the number of reflections in the "EXPNAM".REFMhh reflection file.

```
('HST hhCOS2TM',F10.5)COS2TM
```

For single crystal x-ray diffractometers equipped with a monochromator, the value of $\cos 2\Theta_m$. It is used to calculate the Lorentz-polarization correction as part of the single crystal extinction calculation.

```
('HST hhFSQMAX',E15.6)FSQMAX
```

This single crystal data record is written by **SCABS** and is used to format the output of reflection data from **REFLIST**.

```
('HST hhLAMBDA',3F10.5)LAMBDA
```

The values of the x-ray or neutron wavelengths for a CW single crystal experiment. It is used in the extinction calculations.

```
('HST hhO-CHI ',F10.3)CHI0
('HST hhO-OMG ',F10.3)OMG0
('HST hhO-PHI ',F10.3)PHI0
```

These three records give the orientation angles for the crystal as mounted on a single crystal goniometer. They are used in **SCABS** to calculate to orientation matrix in preparation for absorption corrections.

```
('HST hhPSIINT',F10.5)PSIINT
```

Interval in degrees for the ψ-scan. Written by **PSISCNDTA** in **CAD4RD** and read by **SCABS**.

```
('HST hhPSIAmn',9F7.4)(PHIANG(I=1,MPSI)
             n = 1 to MPSI/9
```

The ψ-angles at which the ψ-scan data were measured. This data is associated with crystal element 'm'. There usually are 360/PSIINT values in the list, but some points may be missing for various reasons. This data is written by **PSISCNDTA** in **CAD4RD**, can be edited in **EDTSCAB** in **EXPEDT** and is read and used by **SCABS**.

```
('HST hhPSIVmn',9F7.4)(PHICOR(I=1,MPSI)
             n = 1 to MPSI/9
```

The normalized ψ-scan intensities. This data is associated with crystal element 'm'. There are 360/PSIINT values in the list. This data is written by **PSISCNDTA** in **CAD4RD** can be edited in **EDTSCAB** in **EXPEDT** and is read and used by **SCABS**.

```
('HST hhTRNSLM',2E15.6)TRMX,TRMN
```

The maximum and minimum values for the transmission (1/absorption) for this histogram as computed by **SCABS** which writes this record.

SCD instrument histogram records

These records are unique to TOF neutron single crystal diffractometers (SCD instruments).

```
('HST hh NREFF',I5)NREFF
```

The number of reflections found by **FINDPK** in this histogram. This is the number in the "EXPNAM".REFFhh reflection file.

```
('HST hh NRRMFL',2X,A66)SCDNORMFILE
```

The name of the data normalization file for this histogram of SCD data. This file contains the incident spectra and the detector nonuniformity correction data. This file is written by **DNORMS** and is read by **NORMS**.

```
('HST hh REDHS',A) 'T run at hh:mm:ss on dd-mmm-yy'
```

Date and time that this SCD histogram was introduced into the **GSAS** system. This record is written by **REDHST**.

```
('HST hhCHI   ',F10.3)CHI
```

This record gives the diffractometer setting angle, χ, for this histogram. Data is written by **REDHST** and read by **INSTDAT**.

```
('HST hhDETA'  ,F10.3)DETA
('HST hhDETD  ',F10.3)DETD
```

These records give the nominal 2Θ angle for the SCD detector and the distance of the detector center from the sample. These records are written by **REDHST** and they are read by **INSTDAT**.

```
('HST hhDMPTIM',A)
```

This record is written by **REDHST** and gives the time that this histogram was dumped by the SCD instrument.

```
('HST hhELAPSD',I10)ELAPSD
('HST hhEVENTS',I10)EVENTS
```

These records are written by **REDHST** and gives the elapsed time for the data collection of this histogram and the number of events (counts) in the histogram.

```
('HST hhFILTYP',2X,A8)FILTYP
```

This record is used to differentiate between the several types of SCD histograms that are supported by **GSAS**. The record is written by **REDHST** and read by **INSTDAT**.

```
('HST hhHGMCNT',I10)HGMCNT
```

This is the total count in an SCD histogram, it is written by **REDHST**.

```
('HST hhIRUN  ',I5)RUN
```

The SCD data run number, written by **REDHST**.

```
('HST hhISCALE',F10.5)ISCALE
```

The scaling factor used to place this histogram on the same relative scale as the first histogram in the set. This scale is determined from the ratio of the total monitor count in the first histogram to that of the current histogram. The record is written by **INTEGRATE**.

```
('HST hhMONCNT',I10)MONCNT
```

The total monitor count for this SCD histogram. It is written by **REDHST**.

```
('HST hhOMEGA 'F10.3)OMEGA
```

This record gives the diffractometer setting angle, ω, for this histogram. Data is written by **REDHST** and read by **INSTDAT**.

```
('HST hhPHI   ',F10.3)PHI
```

This record gives the diffractometer setting angle, ϕ, for this histogram. Data is written by **REDHST** and read by **INSTDAT**.

```
('HST hhSCLRnn',I10,A)SCLR,NAME
```

These records contains the scaler data collected with the histogram. They are written by **REDHST**.

```
('HST hhTBIN  ',F10.2)TBIN
```

The record contains the length of a clock tick in microseconds. It is written by **REDHST** and is read by **INSTDAT**.

```
('HST hhTIMDLY',F10.2)TIMDLY
```

The time delay in microseconds before starting the data collection on the SCD instrument. This record is written by **REDHST** and is read by **INSTDAT**.

```
('HST hhTIMEnn',10I6)(TIME(I),I=1,WLNUM)
```

This SCD data record gives the number of clock ticks from the start of data collection to the end of the current bin. The data is written by **REDHST** and read by **INSTDAT**.

```
('HST hhTLIMIT',F10.2)TLIMIT
```

The time at which the TOF data collection scan is stopped on SCD in microseconds. This is identical to TIMDLY+TBIN*TIME(WLNUM). The record is written by **REDHST** and read by **INSTDAT**.

```
('HST hhTOTCNT',I10)TOTCNT
```

The total count in the histogram and monitor spectra for this histogram. The record is written by **REDHST**.

```
('HST hhTZEROS',F10.0)TZEROS
```

This SCD data record contains the total number of neutron pulses which were used to collect this histogram. The data record is written by **REDHST** and is read by **HSTPLOT** which uses it to determine the apparent instantaneous count rate in the area detector on SCD.

```
('HST hhWLMAX ',F10.3)
('HST hhWLMIN ',F10.3)
```

These records give the range of neutron wave lengths used in collecting this histogram. The data are written by **CELLLSQ** when the lattice constants and crystal orientation information are refined.

```
('HST hhWLNUM ',I5)WLNUM
('HST hhXNUM  ',I5)XNUM
('HST hhYNUM  ',I5)YNUM
```

The number of data channels in this histogram in the *x*, *y* and time or wave length directions. These data are written by **REDHST** and read by **INSTDAT**.

Soft constraint histogram records

In the special case of a histogram consisting of expected interatomic distances with esd's the histogram consists of the following three record types. The histogram type is 'RSN '.

```
('HST hh FACTR',G15.6)FACTR
```

The multiplier for the contributions from this histogram to the minimization function. This can be used to control the influence of the "soft constraints" on the refinement. Zero is a permissible value which results in weighting the restraints at approximately the same level as the other data, i.e. it sets the value of FACTR to the goodness-of-fit (reducedχ^2).

```
('HST hh NBNDS',I5)NBNDS
```

The number of expected interatomic distances for this histogram.

```
('HST hhBNDnnn',8I3,2F6.3)
                  IPHAS,ATSER1,ATSER2,ISYM,ILATT,IA,IB,IC,DIST,ESD
             n = 0,NBNDS
```

The expected interatomic distance with esd from atom ATSER1 to ATSER2 after application of symmetry operator number ISYM, the lattice translation number ILATT and the unit cell translations IA,IB and IC.

Single crystal instrument data records

The following records characterize the single crystal diffractometer used in the experiment. Currently **GSAS** is limited to a single instrument description for such instruments. Some of these records are unique to TOF neutron single crystal instruments while others apply to all single crystal instruments.

```
('INST   DFIL',2X,A66)
```

Name of the experiment file upon which the values in the instrument parameter file are based. This record was originally written by **INSTLSQ** when the instrument parameters were last updated.

```
('INST    IFIL',2X,A66)
```

Name of the instrument parameter file which was read into this experiment.

```
('INST   NAME ',2X,A66)NAME
```

A title entered in the instrument parameter file to provide further identification of the file.

```
('INST   RDATE',2X,A66)
```

Date and time of the last instrument parameter refinement.

```
('INST  ATTNww',7F9.0)WAVE,(ATTN(I),I=1,6)
```

The six attenuator coefficients for the CAD4 instrument. There is a set for each of the standard wavelengths (ww = CU, MO, etc.). This record can be edited by **CAD4RD** and is used by that program to correct the reflection intensities upon initial input.

```
('INST  BCHI  ',2F10.3)BCHI,SIGBCHI
('INST  BDETA ',2F10.3)BDETA,SIGBDETA
('INST  BDETD ',2F10.3)BDETD,SIGBDETD
('INST  BOMGA ',2F10.3)BOMGA,SIGBOMGA
```

These data records give the biases on the angles and detector distance needed to establish the true zero points and their estimated errors for the instrument. These data are obtained by least squares refinement of reflection position data obtained from a small standard sample (i.e. a ruby sphere). The data are copied from the instrument parameter file by **GSCDINST** and are read by **INSTDAT**. They are updated by **INSTLSQ** which can be used to modify an existing instrument parameter file or write a new one.

```
('INST  CHID  ',2F10.3)CHID,SIGCHID
```

The angle that the plane containing the detector center and the incident beam makes with the plane normal to the instrument ω axis. This angle is refinable in the program **INSTLSQ**. The record is read by **INSTDAT**.

```
('INST  CHIR  ',F10.5)CHIR
('INST  OMGR  ',F10.5)OMGR
('INST  PHIR  ',F10.5)PHIR
```

The sense of each of the rotation axes χ, ω and ϕ; +1 for right handed rotation and -1 for left handed rotation about the standard coordinate axes with the single crystal goniometer in the reference orientation. The standard coordinate axes are centered at the sample with the x-axis pointing toward the source and the z-axis pointing along the ω axis away from the goniometer drive (usually "up"). The goniometer reference orientation has the ϕ-axis coincident with the ω-axis and the standard z-axis and the χ-axis is coincident with the x-axis. These records are only needed for single crystal histograms.

```
('INST  DETA  ',2F10.3)DETA,SIGDETA
('INST  DETD  ',2F10.3)DETD,SIGDETD
```

The effective 2Θ value and its sigma of the SCD detector center. Refined and written to the instrument parameter file by **INSTLSQ**.

```
('INST  FILTYP',2X,A8)FILTYP
```

The flag differentiating the various SCD data formats.

```
('INST  L1    ',2F10.3)XTALD,SIGXTALD
```

The distance from the source, moderator, to the crystal in millimeters on the SCD instrument. This is the initial flight path length. It is refined and written by **INSTLSQ**.

```
('INST  PHID  ',2F10.3)PHID,SIGPHID
```

The angle of rotation the detector about the line from the crystal to the detector center. This angle is refined and written by **INSTLSQ**.

```
('INST  TBIN  ',F10.3)TBIN
```

Length of a clock tick used for the instrument parameter data collection. Written by **INSTLSQ**, normally not used elsewhere.

```
('INST  TZERO ',F10.3)TZERO
```

The zero-time offset for SCD data. This value is refined by **INSTLSQ** which writes it to the instrument parameter file.

```
('INST  WLBOX ',I5)
```

A flag defining the type of time binning used for SCD data.

```
('INST  XBIAS ',2F10.3)XBIAS,SIGXBIAS
('INST  XWDTH ',2F10.3)XWDTH,SIGXWDTH
('INST  YBIAS ',2F10.3)YBIAS,SIGYBIAS
('INST  YHGT  ',2F10.3)YHGT,SIGYHGT
```

The SCD detector miscentering and height and width values and their sigmas. These values are refined by **INSTLSQ** which writes them to the instrument parameter file.

```
('INST  XNUM  ',I5)XNUM
('INST  YNUM  ',I5)YNUM
```

These nominal values of XNUM and YNUM are the values for the last experiment used to revise the instrument parameter file. They were written by **INSTLSQ** to the instrument parameter file and copied to here by **REDHST**. It may have been rewritten by **INSTLSQ**.

Constraint records

The next set of records are the constraints relating the parameters to the set of variables actually refined by the least squares. These constraints are edited by routines called by each of the parameter editing routines in **EXPEDT**.

```
('LEQV ccccc  ',10I5)EQVNO,(NREC(I),I=1,EQVNO)
```

This record gives the number of equivalence constraints and the number of terms each for the overall parameter cccc. The overall parameter names are 'ABSC ', 'BKnn ', 'DIFA ', 'DIFC ', 'EXTP ', 'EXTn ', 'FP c ', 'FPPc ', 'HSCL ", 'LAM1 ', PFnn ", POLA ', 'PRFO ', 'RMTN ", 'SCAL ', 'KRAT 'and 'ZERO '.

```
('LEQV ccccnnm',3(2X,A8,F10.3))(CONSTR(I),VALUE(I),I=1,NEQV)
            n = 1 to EQVNO and m = 1 to NREC(n)
```

These records give the individual constraint terms for the overall parameter cccc, where CONSTR is a character string giving the range of histograms (as 'h') or phases and histograms (as 'p,h') whose overall parameters 'cccc' are to be constrained and VALUE is the coefficient. Allowed strings for 'p' and 'h' are 'a' for a single histogram or phase, 'a:b' for a sequence from 'a' to 'b' where 'a' and 'b' are integers and 'ALL' for all histograms or phases. For example '2:4,ALL' refers to phases 2 through 4 for all histograms. In the case of 'RMTN' constraints, CONSTR is the character string `'p     RMij'`, where 'p' is the phase number and 'ij' is the reciprocal metric tensor indices for the element to be constrained.

```
('LEQV HOLDBhh',6(2X,A8))(PNAM(I),I=1,N)
```

This record gives the parameter names of any background coefficients for histogram 'h' that are not to be refined. A maximum of six background coefficients can be held constant for each histogram.

```
('LEQV HOLDL p',6(2X,A8))(PNAM(I),I=1,N)
```

This record gives the names of any reciprocal metric tensor elements for phase 'p' that the user requires to be fixed beyond those that are fixed by symmetry.

```
('LEQV HOLDpnn',6(2X,A8))(PNAM(I),I=1,N)
             n = 1,(NHOLD-1)/6+1
```

These records list those atom parameters for phase 'p' that the user requires to be fixed beyond those that are to be fixed by symmetry.

```
('LNCNnnnnmmmm',2X,4(A8,F8.4))((PNAM(I,J),CNST(I,J),J=1,NTRM),
                                    I=1,NCON)
         n = 1 to NCON and m = 1 to (NTRM-1)/4+1
```

where NCON is the number of constraints, NTRM is the number of terms in each constraint, PNAM is the parameter name and CNST is the coefficient. The parameter name is constructed from the phase, atom numbers and the individual variable name. For example, `'1   2FRAC'`, refers to phase 1, atom 2 and atom fraction.

ORTEP records

The next set of records are written by **ORTEP** and hold the last set of atoms and bonds to be drawn by that program for phase 'p'.

```
('ORTp   NATOM',I5)NATOM
```

The number of atom designator codes to be found on the `'ORTp   ATMSnn'` records.

```
('ORTp   NBOND',I5)NBOND
```

The number of bond descriptor records to be found on the `'ORTp   BONDnn'` records below.

```
('ORTp  ATMSnn',6F10.0)(ADR(I),I=1,NATOM)
             n = 1,(NATOM-1)/6+1
```

The atom designator codes for the atoms to be drawn by **ORTEP**. An atom designator code 'aaacccss' is composed of three parts; the first, 'aaa', is an atom serial number, the second, 'ccc', is the unit cell designators along a,b and c for the location of the atom and the third, 'ss', is a symmetry operator designator.

```
('ORTp  BONDnn',5I5,3F10.4)IOR1,IOR2,ITAR1,ITAR2,IBOND,DMIN,DMAX,RADI
             N = 1,NBOND
```

A bond descriptor record. The bond starts at atom serial numbers IOR1 to IOR2 and ends at atom serial numbers ITAR1 to ITAR2, the bond is drawn with twice IBOND lines over the range of DMIN to DMAX bond lengths using a stick of RADI Å in radius.

Rigid body records

The next set of records occur when a rigid body is described as part of the structural model in any of the phases. These begin with descriptions of the rigid bodies in Cartesian space and are independent of the crystal structure in which they occur.

```
('RGBD  NRBDS  ',I5)NRBDS
```

The number of rigid bodies to be described.

```
('RGBD n NATR ',I5)NATR
```

The number of atoms in rigid body 'n'.

```
('RGBD n NBDS ',I5)NBDS
```

The number of times this rigid body is used in all phases.

```
('RGBD n NSMP ',I5)NSMP
```

The number of translation operators (symmetry parameters) needed to build the rigid body.

```
('RGBD nmPARM ',F10.5,2I5)SDIST,IVAR,IDAMP
        m = 1,NSMP
```

The magnitude of the translation operator 'm', the variable number in the least-squares matrix and damping flag. The variable number can be either unique or the same as another translation operator magnitude in which case they will be taken as the same least squares variable.

```
('RGBD nmSCiii',3F10.7)TRX,TRY,TRZ
             i = 1,NATR and m = 1,NSMP
```

Three translation operators on Cartesian xyz axes for atom 'i', these are multiplied by SDIST from the associated `'RGBD nmPARM '` record to give the new atom location in Cartesian coordinates. The NSMP translation operators are successively applied to the NATR atoms to complete the rigid body. Each of the NSMP operations has its own SDIST multiplier, least-squares matrix location and damping factor.

The rigid bodies defined in Cartesian space are placed in crystallographic space for each phase where needed by the following records.

`('RGBDpn  NBDS',I5)NBDS`

The number of times rigid body type 'n' occurs in phase 'p'.

`('RGBDpnr  NDA',I5)NDA`

The atom sequence number for the first atom of rigid body 'r'. All atoms in a rigid body are stored in the experiment file in sequential locations. There must be 'NATR' atoms in the atom list with serial numbers in sequence starting with 'NDA'. These atoms can not be part of any other rigid body.

```
('RGBDpnr BDFL',9I5,9I1)
                  (IBDORI(I),I=1,6),(IBDLOC(I),I=1,3)(IDAMP(I),I=1,9)
```

Least-squares matrix locations, variable numbers, for the six rotational variables and the three translational variables and their respective damping flags. The variable numbers are normally unique, but they may be the same as the variable numbers for another variable of the same type in which case they will contribute to the same terms in the least-squares matrix and have the same shifts are applied to each of them.

`('RGBDpnr BDLC',3F10.7)BDLOC(I),I=1,3)`

Three fractional unit cell coordinates for the location of the rigid body origin. The IBDORI codes are used to control their inclusion in the least-squares matrix.

`('RGBDpnr BDOR',6(F8.3,I2))(BDORI(I),JAXIS(I),I=1,6)`

The six rotations and their respective axes about the rigid body origin. These rotations operate on the Cartesian coordinate system associated with the rigid body. The axes are the three reference axes x,y and z represented by 1,2 and 3, respectively. The reference coordinates are coincident with the unrotated rigid body Cartesian coordinate system and are aligned with the crystallographic coordinate system so that *x* is parallel to *a*, *z* is parallel to *a*x*b* and *y* is parallel to (*a*x*b*)x*a*. The atomic coordinates are then generated by applying the six rotations to the rigid body coordinates, transforming the result to crystallographic fractional coordinates and finally placing origin of the rigid body at BDLOC in the unit cell.

`('RGBDpnr LSTF',I5)LSTF`

The thermal motion model flag. If it is zero the thermal motion for each atom in the rigid body is represented by either one U_{iso} or six u_{ij}. Those parameters are given with the atom coordinates on the `'CRSp  ATmmmB'` records. If LSTF is 1 then the thermal motion for the entire rigid body is represented by the TLS tensor which is given on the next set of records.

`('RGBDpnrTLSF1',20I3)(ITLS(I),I=1,20)`

Least-squares matrix locations for the six T and L matrix variables and the eight S variables. The variable numbers are normally unique, but they may be the same as the variable numbers for another variable of the same type in which case they will contribute to the same terms in the least-squares matrix and have the same shifts are applied to each of them. These values are not checked by GSAS for consistency with constraints which arise due to crystallographic symmetry.

```
('RGBDpnrTLSP1',6F8.4,2F8.2)(TLS(I),I=1,8)
('RGBDpnrTLSP2',4F8.2,4F8.4)(TLS(I),I=9,16)
('RGBDpnrTLSP3',4F8.4)(TLS(I),I=17,20)
```

The six T matrix elements, the six L matrix elements and the 8 unique S matrix elements for the thermal libration tensor for the rigid body. The format changes are to accommodate the different scales of values for the three matrices. The T matrix elements are in Å^2, the L matrix elements are in degrees^2 and the S matrix is in degree-Å.

The last record

```
('ZZZZZZZZZZZZ  Last EXP file record')
```

This is the last record in any experiment file. Its presence is checked each time the file is opened by any program in **GSAS**. If it is absent the program terminates with an error because the integrity of the file is questionable.

Handling of EXPNAM.EXP File by GSAS

When the experiment file is opened by one of the routines in **GSAS** that is capable of extensively modifying its contents (**EXPEDT** or **GENLES**), a new version is usually produced. The new version is then modified either interactively (as by **EXPEDT**) or updated (as by **GENLES**) to reflect the new values. The next routine in **GSAS** to access the experiment file then opens this new version. In essence these two routines in **GSAS** operate on the experiment file in much the same way as many system routines (e.g. EDIT/EDT in VMS or vi in UNIX). The other routines that only slightly modify the contents of the experiment file (i.e. **FOURIER**, **POWPREF, ORTEP**) and those that just read the contents (i.e. **POWPLOT**, **FORPLOT**) do not make new versions.

EXPNAM.REFnnx - The Reflection Files

These are files which contain a set of reflections for each histogram entered in the experiment file. The filename extension contains the histogram number 'nn' and a letter 'x' indicating the type of reflection information in the file. For powder data 'x' is 'P', for single crystal data 'x' is 'S', for **FINDPK** output reflections 'x' is 'F' and for merged single crystal data 'x' is 'M'. It is an unformatted direct access file; each record contains up to 36 data items.

For powder data there are 18 data items stored for each reflection

DATA(1) = HKL(1)	h index
DATA(2) = HKL(2)	k index
DATA(3) = HKL(3)	l index
DATA(4) = MUL	reflection multiplicity
DATA(5) = ICODE	reflection code
DATA(6) = PRFOCOR	preferred orientation correction
DATA(7) = DSP	d-spacing
DATA(8) = LAM	incident wavelength
DATA(9) = FOSQ	observed F_o^2
DATA(10) = SIGFO	esd in F_o^2
DATA(11) = FOTSQ	F_o^2 corrected for extinction and on scale of F_o^2
DATA(12) = FCSQ	F_c^2 with scale and extinction applied
DATA(13) = FCTSQ	F_c^2 on absolute scale
DATA(14) = PHAS	phase angle for reflection (0-360˚)
DATA(15) = TRANS	transmission factor
DATA(16) = EXTCOR	extinction correction
DATA(17) = PROFLP	sum of profile function
DATA(18) = TOF	time-of-flight

For powder data **POWPREF** writes the front, center and ending TOF or 2Θ for each reflection in DATA(11)-DATA(13); these are overwritten by **GENLES** for those reflections that fall within the powder pattern. The reflection code, ICODE, contains flags indicating the status of the reflection. For refinement ready powder data it is

ICODE = IPHAS*1000 + ILAM*100 + 10*NUCORMAG + IUSE

where

IPHAS is the number of the phase for the reflection,
ILAM is wavelength flag
    =0 for TOF data or reflections arising from radiation of wavelength LAM1
    =1 for wavelength LAM2
NUCORMAG is a flag indicating the status of a magnetic reflection
    =1 space group allowed rmagnetic reflection
    =2 space group extinct magnetic reflection
IUSE is a flag giving symmetry information about F_o
    =1 for space group allowed reflections
    =2 for space group extinct reflections

For single crystal diffraction data ('x' is 'S') all 36 data items in the following list are used, for merged ('x' is 'M') only the first 22 items are used and for **FINDPK** data ('x' is 'F') only the first 21 are used.

DATA(1)	= HKL(1)	h index
DATA(2)	= HKL(2)	k index
DATA(3)	= HKL(3)	l index
DATA(4)	= MUL	reflection multiplicity
DATA(5)	= ICODE	reflection code
DATA(6)	= INCDNT	incident intensity for reflection position on TOF area detector
	= PSI	ψ angle for data from a standard 4-circle instrument
DATA(7)	= DSP	d-spacing
DATA(8)	= LAM	incident wavelength
DATA(9)	= FOSQ	observed F_o^2
DATA(10)	= SIGFO	esd in F_o^2
DATA(11)	= FOTSQ	F_o^2 corrected for extinction and on scale of F_o^2
DATA(12)	= FCSQ	F_c^2 with scale and extinction applied
DATA(13)	= FCTSQ	F_c^2 on absolute scale
DATA(14)	= PHAS	phase angle for reflection (0-360˚)
DATA(15)	= TRANS	transmission factor
DATA(16)	= EXTCOR	extinction correction
DATA(17)	= WTFO	weight for F_o^2 used in least squares
DATA(18)	= TOF	time-of-flight
	= PHI	diffractometer angle for crystal orientation
DATA(19)	= XDET	X detector position on TOF area detector
	= CHI	diffractometer angle for crystal orientation
DATA(20)	= YDET	Y detector position on TOF area detector
	= OMEGA	diffractometer angle for crystal orientation
DATA(21)	= PEAK	single crystal integrated intensity
DATA(22)	= TBAR	absorption weighted mean path through the crystal
DATA(23)	= PKFRAC	fraction of peak included in the integration of SCD data
DATA(24)	= SIGMAI	esd on PEAK
DATA(25-27)	= SCR1	incident beam direction
DATA(28-30)	= SCR2	scattered beam direction
DATA(31-33)	= FAMAG	Real part of the magnetic structure factor
DATA(34-36)	= FBMAG	Imaginary part of the magnetic structure factor

For single crystal data of all types the reflection code is

ICODE = IPHAS*10000 + IELEM*1000 + IMAG*100 + IFRD*10 + IUSE

where

IPHAS is the number of the phase for the reflection
IELEM is the crystallite element number
IMAG is a flag indicating the status of a magnetic reflection
    = 1 space group allowed magnetic reflection
    = 2 space group extinct magnetic reflection
IFRD is a Friedel pair flag
    = 1 for reflection with "standard indices"
    = 2 for the Friedel related reflection
IUSE is a flag indicating the status of a nuclear or x-ray reflection
    = 1 for space group allowed reflections
    = 2 for space group extinct reflections
    = 3 space group allowed magnetic reflection with fractional indices
    = 4 space group extinct magnetic reflection with fractional indices

This file is opened by **OPNREFx**, written by **WRTREFx** and read by **REDREFx** where **x** is **P**, **S** or **F**. The 'M' type files are opened, read and written by the **'S'** routines.

EXPNAM.Phh - The Histogram Files

There is a histogram file 'EXPNAM.Phh' for each powder histogram in the experiment file, and the value of hh matches the histogram number. These files are blocked, unformatted, direct access files; each "record" consists of

ICODE	profile point status code
T	time of flight in µsec or 2Œ in centidegrees. The position is the center of the channel for TOF data.
YO	total observed intensity
YC	calculated intensity excluding fixed background
YI	incident intensity
YB	fixed background intensity
YW	weight
CW	channel or step width in same units as T
IOVLP	reflection range code

The profile point status code is a bit pattern with the following definitions

BIT(0)	- 1	profile point has only background intensity
BIT(0)	- 0	profile point has reflection contributions
BIT(1)	- 1	profile point is in excluded region
BIT(1)	- 0	profile point is in usable region
BIT(2-10)	- 1	profile point coincides with reflection position
BIT(2-10)	- 0	profile point not at reflection position

The bit number for the peak position markers, BIT(2-10), are IPHAS+1. These are used by the plotting program, **POWPLOT**, to mark the reflection positions for each phase. These codes are generated by **HSTPROC** and **HSTMACH** in **POWPREF**.

The reflection range code, IOVLP, is given by

```
IOVLP = CHIGH*16384 + CLOW
```

where CLOW and CHIGH are the first and last, respectively, reflection numbers that contribute to the profile point. These are determined by **HSTMACH** in **POWPREF**. Obviously, the reflections that contribute may come from different phases; they are all mixed together in ascending order of TOF or 2Θ of their leading edges in the reflection file.

These "records" are entered into an array by **WRITPRF**; when full the block is written to the histogram file. Similarly, the "records" are read from the array by **READPRF**; if a requested "record" is not in the current array a new block is read from the file.

EXPNAM.CMT - Variance-Covariance File

The variance-covariance information required by **DISAGL** is written as a sequential unformatted file by **WRCOVAR**. It is read by **RDCOVAR**. These routines also open this file. The old version of this file, if it exists, is deleted by **WRCOVAR** and a new one is created and written. The file consists of three large logical records each of which is described below.

```
NCYCLE,NUMPAR,(PARNAMS(I),I=1,NUMPAR),NUMVAR,(VARNAMS(I),I=1,NUMVAR)
```

The first logical record contains the least squares cycle number, the number of refinable parameters and their names, and the number of resulting least squares variables and their names. The number of variables can be less than the number of parameters because some parameters may be made equivalent by symmetry or user constraints.

```
MATSIZ,(AMAT(I),I=1,MATSIZ)
```

The second logical record contains the size of the variance-covariance matrix and its elements.

```
NCNSTS,(IJCNMT(I),CONMAT(I),I=1,NCNSTS)
```

The third logical record contains the number of non-zero elements in the combined symmetry and user constraint matrix, their indices and associated values. This is a sparse matrix description where only those elements with explicit non-zero values are given; the other elements are omitted.

EXPNAM.fmp - Fourier Map Files

The Fourier map files are unformatted direct access files written by **FOURPRT4** during the calculation of the maps by **FOURIER**. There is one of these for each possible kind of map; they have different extensions. The extensions are FOBS, FCLC, DELF, PTSN and DPTN which correspond to the available map types. **FOURPRT4** also opens these files; any old version is deleted and a new one written. They are read by **REDFMP** as part of **FORPLOT**, **FORPLT** in **PLOTTER** and **FRSHR** in **FORSRH**. These files consists of two header records followed by a set of data records, one for each map 'slice'.

```
NAME,MAPTYP,(CELL(I),I=1,7)
```

The first header record contains a 66 character title, the map type (FOBS, etc.) as a 4 character code (also used for the extension), and the lattice parameters and unit cell volume. This record is skipped by **REDFMP**, all other routines read it.

```
(NXYZI(I),I=1,3),(NXYZO(I),I=1,3),(NXYZT(I),I=1,3),
                    MSECT,NRHO,RMAX,RMIN,SRHO
```

The second header gives the number of steps along the cell edges, the starting step position, the number of steps computed, an orientation flag and the number of density values per slice. The last three values are the maximum and minimum density and the sum of all the density values in the map. The step information is presented as for a hypothetical map section with the first value for across the map, the second value down the map and the third value for section to section. The orientation flag indicates which crystallographic axis is not in the sections.

```
(RHO(I),I=1,NRHO),ROMX,ROMN
```

This record contains the NRHO density values for a section and the maximum and minimum density in the section. There is one of these records for each section in the map.

GSAS Standard Powder Data File

The input powder data file for **GSAS** is a direct access, fixed record length file. It contains a few header records followed by blocks of data each corresponding to an individual powder pattern. Each block is preceded by its own header. All records must be 80 characters in length. The main header has one or two records:

```
(80A)TITLE
```

A title record is first; the information is used by **GSAS** for titles only. **GSAS** can only use the first 66 characters of this record but it must be filled out to 80 characters.

```
('Instrument parameter',60A)FNAME
```

An optional record that must start with the 20 characters shown followed by the instrument parameter file name. If this record is omitted, **GSAS** requests this file name from the user in **EXPEDT**.

Then follows a number of data blocks each beginning with a header. The header record is in free format and has different forms depending on the type of data that follows it. For standard type data the header is:

```
('BANK',3I,A,4F,' STD')IBANK,NCHAN,NREC,BINTYP,(BCOEF(I),I=1,4)
```

The fields are separated by spaces and 'BANK' must be upper case. IBANK is the bank number; if it is zero the data block is from the incident beam monitor. The value of IBANK must be unique within a data file. For TOF data the value of IBANK must corrrespond to the bank number found in the instrument parameter file for the detectors which produced the data. This correspondence is not needed for CW data. NCHAN is the number of data points in the block of data and NREC is the number of records. There are 10 data points per record so NREC is NCHAN/10 rounded up. The value of BINTYP depends on the way the stepwidths are determined. This format is suitable only when the esd associated with each profile point can be calculated directly from the given intensity (i.e. $\sigma_I = \sqrt{I}$). If the esd can not be obtained in this way, then one of the other data formats which explicitly input the esd should be used (see below).

If BINTYP is 'CONST' then the data has a constant stepwidth; BCOEF(1) is the offset for the first step and BCOEF(2) is the stepsize, both in microseconds or centidegrees. If BINTYP is 'LOG6' then the data has a specific logarithmic scaling for the stepwidth; BCOEF(1) is the offset in microseconds and BCOEF(2) is either 102.4 or 409.6 which is the allowed stepsize increment for the Los Alamos Model 6 TOF clock. If BINTYP equals 'TIME_MAP' then a complete time map which defines the step sizes and positions is read from another section of this file (see below) and BCOEF(1) is the number of the time map to be read. If BINTYP is 'LPSD' then BCOEF(1) is the nominal 2Θ value in centidegrees for the linear position sensitive detector (LPSD), BCOEFF(2) is the channel number for this 2Θ angle, and BCOEF(3) is the width of one channel in centidegrees at this position.

Usually CW data has BINTYP equal to 'CONST' or 'LPSD' and TOF data can be any one of the BINTYP's mentioned above except 'LPSD'.

This header is followed by 'NREC' records containing the data in the following format.

```
(10(I2,F6.0))(NCTR(I),YO(I),I=1,NCHAN)
```

where NCTR is the number of counters used to collect the data for each step and YO is the number of counts per counter observed. If NCTR is zero or missing then it is assumed to be one.

The first alternate form for the header is designed to handle data which has been corrected for some instrumental effects (incident intensity, absorption, etc.) so that the weights can no longer be derived directly from the intensities. The header is:

```
('BANK',3I,A,4F,' ESD')IBANK,NCHAN,NREC,BINTYP,(BCOEF(I),I=1,4)
```

As above the value of IBANK must be unique within a data file. Each data point consists of the intensity and an esd for that intensity. Thus there are 5 data points per record and NREC is NCHAN/5 rounded up. The values of BINTYP and BCOEF are the same as described for the standard data header.

The data records are in the following form:

```
(10F8)(YOT(I),YE(I),I=1,NCHAN)
```

where YOT is the intensity and YE is the esd for YOT. The decimal point must be given to force its proper placement in these values.

The second alternate form for the header is designed to handle data which has been collected on a diffractometer where the steps between values is somewhat uneven (e.g. TOF data collected on the diffractometers at the ISIS Facility, Rutherford-Appleton Laboratory, UK) The header is:

```
('BANK',3I,A,4F,' ALT')IBANK,NCHAN,NREC,BINTYP,(BCOEF(I),I=1,4)
```

As above the value of IBANK must be unique within a data file. For TOF data the value of IBANK must corrrespond to the bank number found in the instrument parameter file for the detectors which produced the data. This correspondence is not needed for CW data. Each data point consists of the TOF, intensity and an esd for that intensity. Thus there are 4 data points per record and NREC is NCHAN/4 rounded up. The values of BINTYP and BCOEF are the same as described for the standard data header with the addition of BINTYP = 'RALF' which forces the use of the TOFT values below for the positions. In this case BCOEF(1) is the starting TOF in μsec*32, BCOEF(2) is the width of the first step in μsec*32, BCOEF(3) is the start of the log scaled step portion of the data in μsec*32 and BCOEF(4) is the resolution to be used in approximating the size of each step beyond BCOEF(3).

The data records are in the following form:

```
(4(F8.0,F7.4,F5.4))((TOFT(I),YOT(I),YE(I),I=1,NCHAN)
```

where TOFT is in microsteps (TOF in pulses of width CLCKWDT times 32 or centidegrees times 32), YOT is the normalized count and YE is the esd for YOT. Normally the decimal point is left off the values and the format statement properly scales the values.

A time map is included in the file by starting with the following header:

```
('TIME_MAP',3I,A,F)MAPNO,NVALS,NREC,'TIME_MAP',CLCKWDT
```

The fields are separated by spaces and 'TIME_MAP' must be uppercase. MAPNO is the time map number. NVALS is the number of data items in the time map; there are three for each point in the map. NREC is the number of records which is NVALS/10 rounded up. CLCKWDT is in number of clock pulses per μsec.

This header is followed by NREC records which contain the time map information.

```
(10I8)((TMAP(J,I),J=1,3),I=1,MAXMAPU),TMAX
```

where MAXMAPU is NVALS-1, TMAP is a triplet of time map values and TMAX is the maximum allowable TOF. The three time map values are starting channel number, TOF in pulses of width CLCKWDT for the front of the channel and the channel width in pulses. Each change in the channel width in the data set has a corresponding entry in the time map; the entries are in ascending order of channel number. Currently there are 1024 entries allowed for the time map in **GSAS**.

These sets of header record plus data records may be repeated in any order until the entire data set for the experiment is included in the file. This file is processed by **HSTREAD** for **POWPREF** and **READHST** for **EXPEDT**; the data header records are interpreted by **EXTRBNK**, the data records are read by **GETRAWPT** and the time map is read by **REDTMAP**.

ATOMDATA.DAT - Atom Data File

The characteristic atomic information (scattering factors, absorption coefficients, etc.) are stored on a formatted ISAM file. Each record is 80 characters long and starts with a 12 character key which is used by **GSAS** to fetch that record from the file. The information on the record is read as a 66 character block by **TYPINS** and written unchanged on to the 'AFAC' records in the experiment file. The file is arranged so that all information for a given element is in one place on four different kinds of records. A description of each kind follows. There are several records at the beginning of the file listing the various references used to accumulate the data.

```
('zz aaaa     ',9F7.0)(SCFC(I),I=1,9)
   z = atomic number, a = element symbol
```

This record holds x-ray scattering factor coefficients (a_i, b_i and c) as listed by Cromer & Waber (1974), International Tables for X-ray Crystallography, Vol. IV, p 99-101. The atomic number is an integer in the range 1-99; this is the same for all records for a given element. The element symbol consists of the standard two letter chemical symbol (upper case) and the valence as a sign and a numerical value, e.g. 'TI+4', if necessary. There is always one of these records for every element giving the neutral atom scattering factors; some elements also have ionic scattering factors. The atomic scattering factor is then calculated by

$$f = c + \sum_{i=1}^{4} a_i e^{-b_i \sin^2\theta/\lambda^2}$$

```
('zz aa_nnn   ',F7.0,4F6.0)WT,BLEN,BILEN,RNMU,RNMUX
```

The isotopic data for 'aa_nnn' where 'aa' is the chemical symbol (upper case) and 'nnn' is the isotope. The data are isotopic weight, real and imaginary neutron scattering lengths, and the wavelength dependent and wavelength independent neutron absorption cross sections. If 'nnn' is blank then the data are for the natural abundance element. Synthetic elements do not have 'natural abundance' data. There may be several of these records for a given element. The values are taken from Koster & Yelon, (1982), Neutron Diffraction Newsletter.

```
('zz aa_SIZ   ',2F10.2,F5.2,I5)DRAD,ARAD,PRAD,COLOR
```

This record contains default atom size data for distance/angle calculations and for the structure plotting programs.

```
('zz aa_XAB   ',1X,5F6.0)(RXMU(I),I=1,5)
```

The x-ray absorption cross sections for Cr, Fe, Cu, Mo and Ag Kα radiation, respectively. These values are taken from Hubbell, McMaster, Del Grande & Mallett (1974), International Tables for X-ray Crystallography, Vol. IV, pp 55-66.

```
('zz aa_XAN   ',1X,10F6.0)(XFP(I),XFPP(I),I=1,5)
```

The real and imaginary parts (f' and f") of the anomalous dispersion for Cr, Fe, Cu, Mo and Ag Kα radiation, respectively. These values are taken from Cromer & Ibers (1974), International Tables for X-Ray Crystallography, Vol. IV, pp 149-150.

Instrument Parameter File

The instrument parameter file is formatted the same way as the experiment file (see above) with 80 or less character records and a 12 character key. The information on this file is the characteristic data for the instrument used to collect x-ray or neutron diffraction data. It holds the geometric description of the instrument, characteristic intensity spectrum and other specific data. The records are very similar to some of those in the experiment file; only the keys are different. A few records are not used by **GSAS** programs but are needed by local data preparation programs. Nonetheless, some of these records are ultimately copied to the experiment file; this is done in **HSTINS**. What follows is a complete listing of the records in an instrument parameters file for a TOF powder diffractometer at LANSCE with some from other types of instruments.

The initial set of records characterize the whole instrument and are not copied to the experiment file.

```
('INS   BANK  ',I5)NBANK
```

The number of counter banks on the instrument. Generally NBANK is one for CW instruments; TOF instruments usually have more than one bank of detectors. It can also indicate the number of different configurations used for the instrument (i.e. different x-ray tubes used on the diffractometer). This record is required by **GSAS**.

```
('INS   FPATH1',F10.0)FPATH1
```

The neutron flight path in meters from the source to the sample on a TOF diffractometer. Not needed by **GSAS**.

```
('INS   HTYPE ',2X,A4)HTYPE
```

The histogram type for all data from this instrument; see the description of the ' EXPR HTYPc' record in an experiment file for a full description of histogram types. For powder data the last character of HTYPE must be 'R'; the other characters specify the kind of data. This record is required by **GSAS**.

```
('INS   MONIT ',I5,F10.0,I5,F10.0)MTUB1,MPATH1,MTUB2,MPATH2
```

The spectrum numbers and location of direct beam monitors in meters as measured from the source on a TOF diffractometer. Not needed by **GSAS**.

```
('INS   NSPEC ',I5)NSPEC
```

The number of spectra collected by a LANSCE TOF diffractometer; equal to the number of tubes plus the number of direct beam monitor detectors. Not needed by **GSAS**.

The next section of records contains specific information for a bank of detectors. They are repeated for each of the NBANK detectors on the instrument. Unless stated otherwise they are required by **GSAS**.

```
('INS bb ICONS',3F10.0, 10X,F10.0,I5,F10.0)
                  DIFC,DIFA,ZERO,POLA,IPOLA,KRATIO
       b = bank number
```

These are the diffractometer constants for one bank of detectors on a powder diffractometer. In the case of a TOF diffractometer the constants relate d-spacing and TOF in microseconds. For CW data the same record holds wavelength data, LAM1 and LAM2, in place of DIFC and DIFA. The polarization fraction POLA, the polarization type IPOLA, and the $K_{\alpha2}/K_{\alpha1}$ ratio KRATIO are absent for neutron data.

```
('INS bb IRAD ',I5)IRAD
```

If this instrument is an x-ray single crystal or powder diffractometer, this record is required and has an integer (1 to 5) indicating which characteristic radiation is used; Cr, Fe, Cu, Mo or Ag Ka, respectively. If IRAD is zero then special anomalous and absorption coefficients for each kind of atom will be required when this histogram is used.

```
('INS bbBNKPAR',5F10.0,2I5)DIST,TTHETA,TILT,SEPN,HGHT,NTUBE,ITUBE
```

This record describes a TOF counter bank. This data is mostly used by the program **FSTBUSBIN** to bin the individual spectra from the ^{3}He tubes in a bank into one spectrum. It is not needed for CW instruments.

```
('INS bbBNKTCc',8F7.2)(DIFC(I),I=1,NTUBE)
             c = 1 to 1+(NTUBE-1)/4
```

These are the individual DIFC values for each tube in a bank of detectors; if present this is used by **FSTBUSBIN** in preference to the data on the previous record. They are not needed for CW instruments and not needed by **GSAS** for any instruments.

The next series of records characterize the incident spectrum and are initially defined by the program **FITSPEC**. At least the first two are required for both TOF and CW powder instruments.

```
('INS bbI HEAD',2X,A66)IHEAD
```

A title taken from the incident spectrum raw data file. It can contain "dummy" information.

```
('INS bbI ITYP',I5,2F10.4,I10)ITYP,TMIN,TMAX,CHKSUM
```

The type of incident intensity function, the minimum TOF in msec (or 2Θ in deg), the maximum TOF (or 2Θ) over which the function can be applied and a checksum on the incident spectrum. The latter is used to check if this incident data has been applied to another histogram. For data sets for which there is no fitted incident spectrum, set ITYP to 0, choose appropriate values for TMIN, TMAX and pick a random integer for CHKSUM.

```
('INS bbICOFFc',4E15.6)(VINC(I),I=1,12)
             c = 1 to 3
```

Coefficients for the incident intensity function. For TOF they are expressed in terms of TOF in milliseconds. These records not needed if ITYP is 0.

```
('INS bbIECOFc',4E15.6)(SINC(I),I=1,12)
             c = 1 to 3
```

The esd's for each of the coefficients. These records not needed if ITYP is 0.

```
('INS bbIECORc',10F6.3)(PINC(I),I=1,78)
             c = 1 to 8
```

The elements of the correlation matrix in upper triangular form for the incident intensity coefficients. These with the esd's are used to calculate the esd in the calculated incident intensity at each point in the profile. These records not needed if ITYP is 0.

```
('INS bbPRCFn ',2I5,F10.5)PTYP,NCOF,CTOF
            n = 1,NTYP
('INS bbPRCFnc',4E15.6)(COF(I),I=1,NCOF)
             c = 1 to 1+(NCOF-1)/4
```

These records give the NTYP sets of available profile functions and their default coefficients for data from this bank of detectors. The first record contains the powder profile type , number of coefficients and a cutoff factor. The second and subsequent record (c = 1,...) contain the coefficients with four per record. The first set defines the default profile function type for this instrument, i.e. PTYP for the first set does not have to be 1.