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GSAS

GENERAL STRUCTURE ANALYSIS SYSTEM

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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 all Microsoft operating systems on the Intel based personal computer (MS-DOS 6.x, Windows 95/98/2000 and NT 4.0) and several Unix operating systems (Linux on Intel PC, Silicon Graphics Irix 6.x, and Hewlett-Packard UX). An integral part of GSAS is the facility for interactive graphics display based on the PGPLOT graphical subroutine library. The Unix versions of GSAS support X-windows graphical displays while the Microsoft OS version supports native MS-DOS graphics on the PC. It also supports hard copy graphics devices (PostScript printers and Hewlett-Packard printers and plotters). 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 Microsoft operating systems (MS-DOS, Win95/98/2000 and WinNT4.0) and Intel based Linux (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 PC and Unix platforms on Postscript printers.

GSAS Installation for Microsoft Windows from ftp files:

System Requirements: Intel based PC (486 or better) with Microsoft operating systems MS-DOS 6.x, Windows 95/98/2000 or Windows NT 4.0 (Win95/98 or WinNT4.0 recommended).

The GSAS distribution kit for MS-DOS/Windows consists of a single self-extracting compressed file, which is approximately 50% smaller than the original suite of files. This file needs to be transferred in binary format. There is also a "readme" file that is transferred in ASCII format.

To ensure that the file structure and command files for GSAS are set up appropriately on your PC, we have provided an installation procedure. These instructions cover both the initial installations of GSAS on a PC 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 for you 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. We have assumed that you will be installing GSAS onto the C-drive of your PC. Any other drive may be used, just use the appropriate drive letter. These commands are best done in a DOS window.

1. Create a directory named C:\gsas. Sufficient disk space to hold the system and the distribution kit should be made available (ca. 20Mb).

2. Initiate contact with the distribution machine at Los Alamos with your favorite web browser:

ftp://ftp.lanl.gov/public/gsas

When you get connected to this site you should see the following selection:

```
GSASNEWS.txt      44 Kb    Mon Jul 03 19:20:00 2000 Plain Text
hp-ux/                     Mon Mar 22 00:00:00 1999 Directory
linux/                     Fri Apr 21 15:12:00 2000 Directory
manual/                    Fri Mar 19 00:00:00 1999 Directory
ms-dos/                    Fri May 26 21:44:00 2000 Directory
readme.1st       879 bytes Mon Jul 03 19:22:00 2000
sgi-irix/                  Mon Mar 22 00:00:00 1999 Directory
```

You may read the files ìreadme.1stî and ìgsasnews.txtî on-line or download them to your machine for reading later. Then select the ìms-dosî subdirectory; the following selection will be available:

```
class.zip        550 Kb    Fri May 26 21:44:00 2000 Zip Compressed Data
fprime.zip       310 Kb    Mon Apr 10 19:52:00 2000 Zip Compressed Data
gsaskit.exe     6776 Kb    Mon Jul 03 16:11:00 2000 Binary Executable
pfe7.zip         561 Kb    Thu Mar 18 00:00:00 1999 Zip Compressed Data
readme.txt         2 Kb    Fri Mar 03 22:35:00 2000 Plain Text
vrweb.exe       2272 Kb    Thu Mar 18 00:00:00 1999 Binary Executable
```

Transfer gsaskit.exe to your local \gsas directory. Be sure to do this transfer in ìbinaryî. Also transfer the text file ìreadme.dosî; it contains detailed instructions for installing GSAS in Windows. The file ìpfe7.zipî contains a very useful text editor by Alan Phillips, ìfprime.zipî contains a Windows version of the program by Don Cromer for calculating anomalous dispersion scattering factors (fí and fî) for any element, ì vrweb.exeî contains a stand alone virtual reality display program by Gerbert Orasche and Michael Pichler. The file ìclass.zipî contains a large number of Rietveld refinement exercises.

3. Open a MS-DOS ìconsoleî window on your PC and set the current directory to the directory created in step 1 (e.g. cd \gsas).

4. Execute the self-extracting compressed file.

gsaskit ñd (the ì-dî is important!)

This will expand the distribution kit forming the proper directory structure for GSAS on the PC. The ì-dî option is important; if it is omitted then all the GSAS files are created in the main directory and the system will not run correctly. If you are updating an old version of GSAS, then you may be asked if you want to replace each file. If so, answer ìaî to replace all GSAS files. You can delete gsaskit.exe to recover ~6.8Mb of disk space.

5. Modify your autoexec.bat file as follows (even if it is otherwise empty)

set path=%path%;c:\gsas\exe
set gsas=c:\gsas
set PGPLOT_FONT=c:\gsas\fonts\grfont.dat

6. Reboot your machine. GSAS is now ready to use.

7. For Win95/98 you can create a shortcut to \gsas\exe\pc-gsas.exe and put it in a convenient location such as your desktop. PC-GSAS is a convenient Windows style shell with pull-down menus for accessing the component programs in GSAS. PC-GSAS does not work in the other Microsoft operating systems; use the QBASIC based routine \gsas\exe\gsas.bas instead. The shortcut for this is \gsas\exe\gsas. QBASIC must be made available to your system; if not already installed it can be found in your Microsoft distribution disks.

8. You can also ëregisterí the GSAS experiment files with the Windows operating system. In Windows 98 do the following (Windows 95/NT are similar):

in Windows Explorer select "View" and then "Folder Options"

select "file types" and then select "new type"

for description of type enter: GSAS experiment file

for associated extension enter: exp

select "new"

for action enter: expedt

for application select "browse" and find \gsas\exe\expedt.exe

repeat steps e-g for powpref, genles, powplot, etc. as desired

select "change icon" and then select "browse" and find \gsas\gsas.ico

select "OK" (for icon) and check icon is OK (may have to repeat step i)

select "OK" to finish

Now you will be able to "right click" on an experiment file and select the GSAS routine you want to use. Each experiment file in Explorer will have the GSAS icon.

GSAS Installation on Linux for Intel PC from ftp files:

System Requirements: Linux 6.x. and Intel PC (486 or better).

The GSAS distribution kit for Linux on Intel processors (PC) contains a single large file that is kept in a compressed form and is approximately 50% smaller than the original. This file needs to be transferred in binary format. There is also this "readme" file that is transferred in ASCII format.

To ensure that the file structure and command files for GSAS are set up appropriately on your Linux PC we have provided below a set of installation instructions. 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 (you may use Netscape or other web browser):

    ftp://ftp.lanl.gov/public/gsas

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 [linux] (to change to the Linux distribution directory)
    get readme.linux (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 Linux PC, type the following commands:)

binary (set the mode of transfer)
get gsaskit.tar.gz (transfer the compressed file)
quit (exit ftp)

Next decompress gsaskit.tar.gz and restore the GSAS files. Use the following command to do this:

    gzip ñdc gsaskit.tar.gz | tar xvf - (creates all the gsas files from gsas.tar.Z)

You may now delete gsas.tar.gz to save ~10Mb of disk space.

    rm gsas.tar.gz (delete file)

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

    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 PC version except that Unix style file paths must be used for the exercises. For example, use "/usr/gsas/example/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

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 that is invoked by using the PC-GSAS shortcut (for Win95/98) on your PC or by entering ëgsas’ on your Unix workstation. In the latter case, this shell is capable of filtering the GSAS commands from other Unix commands so that all terminal operations can be done from within the shell. In other words, you are able to do virtually any Unix command from within the GSAS shell.

BIJCALC - Thermal Motion Analysis

BIJCALC 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 reads data measured on the Enraf-Nonius CAD4 instrument, extracting the unit cell information, examining the standard reflections and writing the reflection data into the ëreflection fileí with corrections for crystal decay, etc. as indicated by the standard reflections. It also copies the ψ scan data into the ëexperiment fileí for use in absorption correction calculations.

CLLCHG - Unit Cell Transformation Routine

CLLCHG transforms 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 calculates 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 the first program in GSAS run by the user for input of powder diffraction data. 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 that 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 that 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 ëexperiment fileí and has the name ëexpname.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. For PC and Unix systems only one previous version is retained; it has the name ëexpname.OLDí. A previous ëexpname.OLDí file is overwritten.

EXPNAM – Selection of Experiment Name

EXPNAM invokes the selection of an experiment name, ëexpnameí, for GSAS. The experiment name is limited to an 8 character string containing no spaces. This name is used by GSAS to construct the names of all files associated with the particular problem you are working on. These files will be created within your chosen ìlocalî directory; selection of the local directory must be done before proceeding with any part of GSAS that requires an experiment name.

FITSPEC - Fitting of Incident Spectra

FITSPEC is 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 ëinstrument parameter file'.

FORSRH - Fourier Peak Search

FORSRH is a Fourier peak search routine. It lists peak positions and their heights that are found in the ëFourier map fileí and optionally places them in the ëexperiment fileí for inclusion in distance and angle calculations.

FORPLOT - Fourier Map Display

FORPLOT is a Fourier map display program. It is capable of producing on various graphics devices (same as those supported by EXPEDT) single map slices or interpolated oblique slices of maps generated by FOURIER and stored on ëFourier map files'. FORPLOT is also used for converting the GSAS Fourier map file format into the ëdn6í format used by certain 3D viewing programs such as Swiss PDB Viewer.

FOURIER - Fourier Map Calculations

FOURIER is a 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 ëFourier map fileí intended for input to the peak search routine, FORSRH, and the graphics display program FORPLOT. As an option it can produce a numerical map in the list file.

GENLES - General Least Squares

GENLES is a 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. Alternatively, for large refinement problems (i.e. macromolecules) a band matrix approximation to the full matrix is constructed. It also has facilities for constructing linear constraints between parameters, rigid body constraints for molecular fragments and can include stereochemical observations as ësoft restraints. GENLES outputs a summary of the least-squares results on a list file and generates an updated version of the ëexperiment file'. The previous version of the experiment file is retained as ëexpname.OLDí; the previous ëexpname.OLDí file is overwritten.

GEOMETRY - Calculate Molecular Geometry

GEOMETRY 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.

GSAS2CIF – Prepare Crystallographic Information File

GSAS2CIF prepares a Crystallographic Information File (CIF) suitable for submission to a journal for publication. Currently, GSAS2CIF is under development and the current version should be considered to be a ìbetaî version.

GSAS2PDB – Prepare Protein Data Base File

GSAS2PDB prepares a Protein Data Base file (PDF). The output file name has the extension ì.entî. Currently, GSAS2PDB is under development and the current version should be considered to be a ìbetaî version, however it is sufficiently complete that structure drawing packages such as Swiss PDB Viewer, RasMol and WebLab Viewer can read the output file and usually draw the structure. It can also be used by EXPEDT for reading in atomic coordinates for a macromolecule.

HKLSORT - Reflection Lister for Publication

HKLSORT 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 sections of a ëhistogram fileí or produce a list file of the entire powder pattern in a form suitable for deposit with a journal.

ISTATS - Intensity Statistics

ISTATS can be 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.

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 Bruker P3R3 single crystal instrument, extracting the unit cell information, examining the standard reflections and writing the reflection data into the ëreflection fileí with corrections for crystal decay, etc. as indicated by the standard reflections. It also copies the ψ scan data into the ëexperiment fileí for use in absorption correction calculations.

POLFPLOT – Pole Figure Plotting

POLFPLOT displays pole figures on various graphics devices. POLFPLOT generates the pole figures from the spherical harmonic coefficients obtained *via* Rietveld refinement of powder diffraction data. POLFPLOT can also prepare axial distribution plots and prepare pole figure data files suitable for further processing by the popLA system of texture analysis programs.

POWPLOT - Powder Pattern Plotting

POWPLOT displays powder diffraction patterns on various graphics devices. It is capable of showing 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 ëreflection fileí and a ëhistogram fileí 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 that are suitable for publication purposes.

RAWPLOT - Plotting of Powder Patterns

RAWPLOT displays powder diffraction data in either d-spacing or data collection units (2Θ, time-of-flight, or energy). RAWPLOT also has facilities for fitting a set of individual reflections for their position, intensity and profile shape coefficients. The results of this fitting can be out put to a separate listing file for input to other analysis programs (e.g. pattern indexing routines). The input data must be in the GSAS standard raw data file format and an ëinstrument fileí is also required.

RCALC - Analysis of Structure Factor Residuals

RCALC is 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. Generally RCALC is of most use for single crystal diffraction data but it can also be applied to reflection structure factors extracted from a powder diffraction pattern in the course of a Rietveld refinement.

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. It can also be used to extract the set of reflections from a single phase in a powder diffraction pattern after a LeBail or Rietveld refinement.

REF2ASC - Conversion Of Reflection File to ASCII

REF2ASC converts GSAS reflection files (single crystal or powder) into an ASCII form suitable for transfer between PC and Unix machines. The ASCII files may also be read by nonGSAS crystallographic software (e.g. MULTAN). (See REF2BIN below).

REF2BIN - Conversion of ASCII Reflection File to GSAS Binary

REF2BIN converts ASCII files created by REF2ASC 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 makes absorption corrections to single crystal data from either X-ray or neutron single crystal instruments.

SCMERGE - Single Crystal Data Sort and Merge

SCMERGE merges single crystal reflection data into a unique set with standardized reflection indices which are written to a new ëreflection 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 ëreflection 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 - General Input of Single Crystal Data

SXTLDATA is a general structure factor input routine for reading single crystal data from an ASCII file that is then put into a standard GSAS format reflection file.

UNIMOL - Assembling of Unique Molecules

UNIMOL assembles unique molecules from the atoms in the ëexperiment 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 ëexperiment file'. One however has the option of rearranging the atom list to suit their needs.

VRSTPLOT – Preparation of Virtual Reality Crystal Structure File

VRSTPLOT prepares a Virtual Reality Modeling Language (VRML Version 1.0) graphics file. VRSTPLOT can produce a drawing file with ball and stick, thermal ellipsoid, space filling or polyhedra representations of a crystal structure. It can also place in the drawing a single density contour from one of the maps produced by FOURIER. The resulting ëexpname.wrlí file is then accessed with a VRML viewer that generally allows a full 3-dimensional exploration of the crystal structure.

Utility Routines in GSAS (Unix only)

There are a number of utility routines in the Unix version of 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. On a PC with Microsoft Windows most of these utilities are not needed as these operations are more conveniently done with native Windows facilities.

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

TEXP is used to list the experiment file on the terminal. DEXP is used to delete all files for the experiment except the experiment and raw data files. WARNING - DEXP should not be used for a single crystal experiment; it <u>will</u> delete all your reflection files! SEXP is used to search the experiment file for a string. LSEXP 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.

NEXT - Experiment Selection Utilities

NEXT selects the next experiment in alphabetical order.

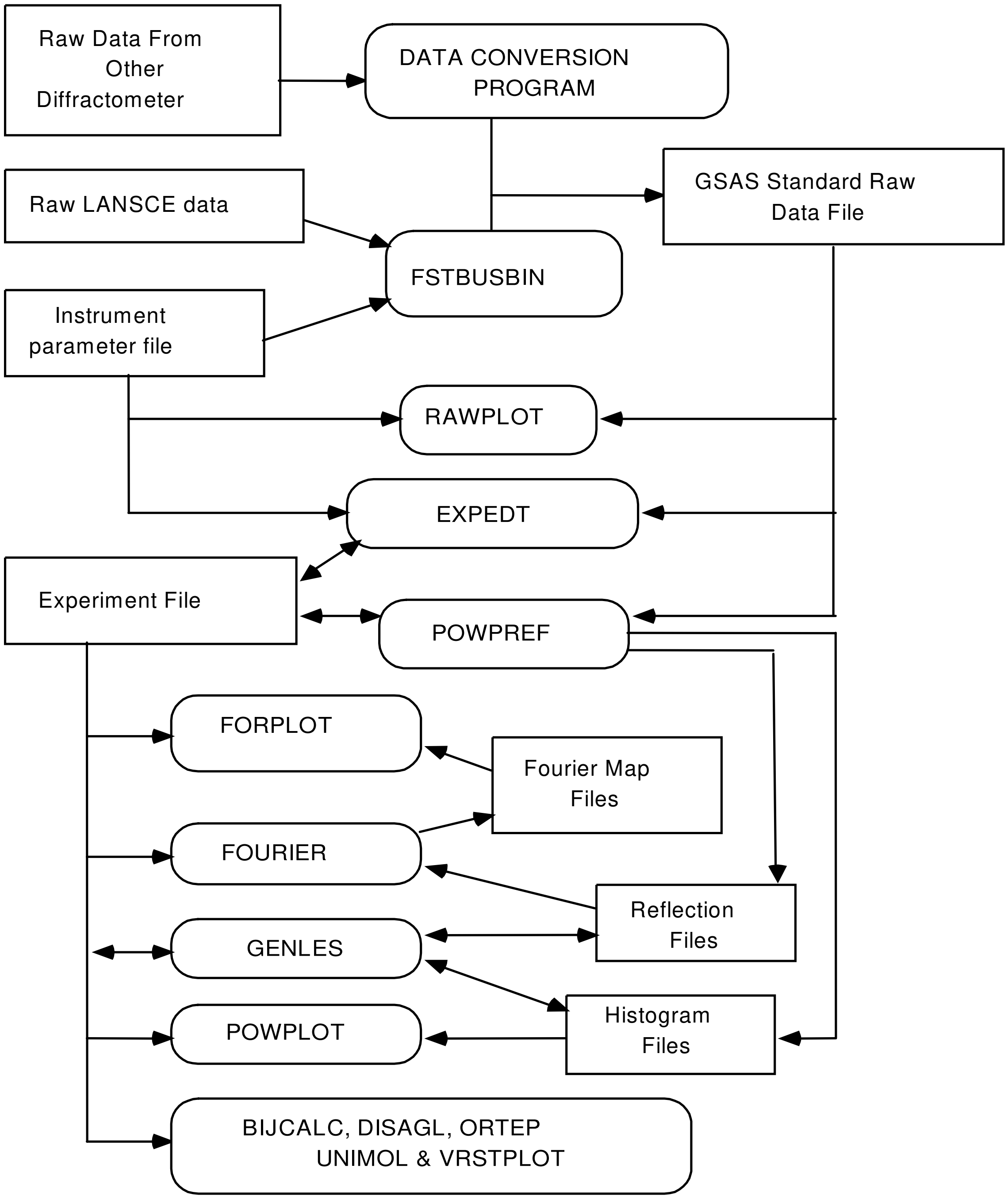
Program Execution in GSAS

For PC systems all programs in GSAS are executed in ìforegroundî mode. In any of the Windows operating systems, a ìDOSî window is created for each executing GSAS routine. When the GSAS routine finishes, you will be prompted for an additional carriage return to terminate the run and close the window. In Win95/98 and WinNT4.0, the GSAS program will continue to execute even if this window is not ìon topî or even minimized. However, this window will not be closed automatically when the GSAS routine finishes; you must still bring it back to your desktop and enter a carriage return to close it.

On Unix systems, the programs in GSAS are assumed to run interactively.

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 four exercises that 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 Rietveld refinement of a typical constant wavelength x-ray powder diffraction data set from a conventional laboratory diffractometer. The fourth 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 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 constant wavelength 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 describes the refinement of the structure of fluoroapatite using conventional laboratory Bragg-Brentano diffraction data collected with CuK_α radiation. The first steps follow those of the previous exercises adapted for typical x-ray powder diffraction data. After the refinement is complete the use of the program VRSTPLOT for producing a VRML drawing of the structure is presented.

The fourth exercise begins with the input using the program CAD4RD of a single crystal x-ray data set of oxonium hexafloroantimonate collected on an Enraf-Nonius CAD4 diffractometer. Preliminary data processing steps of absorption corrections (SCABS), a sort, and a merge of the data (SCMERGE) follow to give the unique reflection set. After this you will calculate a Patterson map with FOURIER. This map is then 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 four exercises. Plan on taking 10-30 minutes for each session with EXPEDT, POWPLOT and FORPLOT. The run times for 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 on most modern computer systems. 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 and then a carriage return ë↵í (most keyboards have ë↵Enterí). 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 ë↵í is given, then 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 ë↵í; at that time the command string 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 ë/í 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 ë/í to accept the remaining defaults. The items in any input list must be separated by spaces, tabs or 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). An alternative input for decimal values in GSAS can be useful when the desired value is some trigonometric value for an angle. If the desired value is the sine, cosine or tangent of some angle then the value may be entered as ës67.2í, ëc67.2í or ët67.2í for sin(67.2), cos(67.2) or tan(67.2), respectively. Negative angles must be converted to positive equivalents before using this input mode.

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 to 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 that are 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 cannot be interpreted, GSAS will usually print the menu help listing at the point of error and the remaining commands on the string are ignored. This ìtype aheadî 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.

Macro capability in GSAS

All programs in GSAS have the capability to both produce and use macro files. This capability allows one to create reusable sequences of GSAS input commands that can be used for repetitive inputs. A macro file is created by entering ë@Mí at any GSAS program prompt. Immediately the program will request the name to be used for the macro file and then the original prompt is repeated. All commands that are subsequently entered are saved in the macro file as one input line per record until either the sequence of commands results in exiting the particular GSAS program or until ë@Qí is entered which closes the macro file. Note that one cannot create a single macro file that spans more than one GSAS routine. Also, macro files cannot be nested. The resulting macro file is an ordinary sequential text file that can be edited if desired. As an extended sequence of GSAS commands jumping from one menu to another is generally quite difficult to interpret by eye, each GSAS input line may contain a comment entered after a ë!í. Thus you can create a commented macro file. Examples of GSAS macro files can be found in \gsas\macros. A macro file is used by entering ë@Rí at the appropriate GSAS prompt. The program will immediately request the name of the macro file to be used and then attempt to execute the sequence of commands in the macro file. Processing of the macro file will continue until all the commands in the file are exhausted. Obviously, using the incorrect macro file or starting one at the wrong place will generally produce errors.

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. MS-DOS, Windows and Unix use very different constructions for directory and file names. In MS-DOS or Windows a file name is of the form ëC:\name1\name2\file.extí while for Unix the structure is more like ë/name1/name2/file.extí (notice that there is no disk letter and the different direction for the ìslashî). MS-DOS and Windows 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. ëstructure.datí is a different file name from ëStructure.dat', so one must exercise care in entering Unix file names in GSAS. A useful trick in Windows is to find the desired file in ìExplorerî, and ìdrag-and-dropî it onto the MS-DOS window that has the GSAS file name prompt. The name will appear as the response to the prompt and a ë↵í is then needed to invoke it. File names for both MS-DOS/Windows and Unix versions of GSAS allow a total of 256 characters for the full file name (path/name.ext). The MS-DOS/Windows path names can include blanks but Unix path names cannot be formed with embedded blanks. File names in GSAS can only be 8 characters (or less) with a 3-character (or less) extension. An experiment name is used to form the file name for all the files generated by GSAS; thus, they can only be 8 characters or less. These generated files are all in upper case, thus the nickel example below will generate the files NICKEL.CMT, NICKEL.EXP, NICKEL.LST, NICKEL.P01, NICKEL.P02, NICKEL.R01 and NICKEL.R02. In the examples below, we will show the Unix name; interestingly, these also work for the MS-DOS/Windows version of GSAS (i.e. with the forward ë/í). The 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 /gsas. If you have installed it elsewhere you will have to modify the path names in these examples as you work them. You may have to include the drive letter as well for the MS-DOS/Windows version if your working directory and the gsas directory are on different disk drives.

Neutron TOF Powder Data - Nickel Powder

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 that will be subject to simultaneous Rietveld refinement.

Introduction to EXPEDT

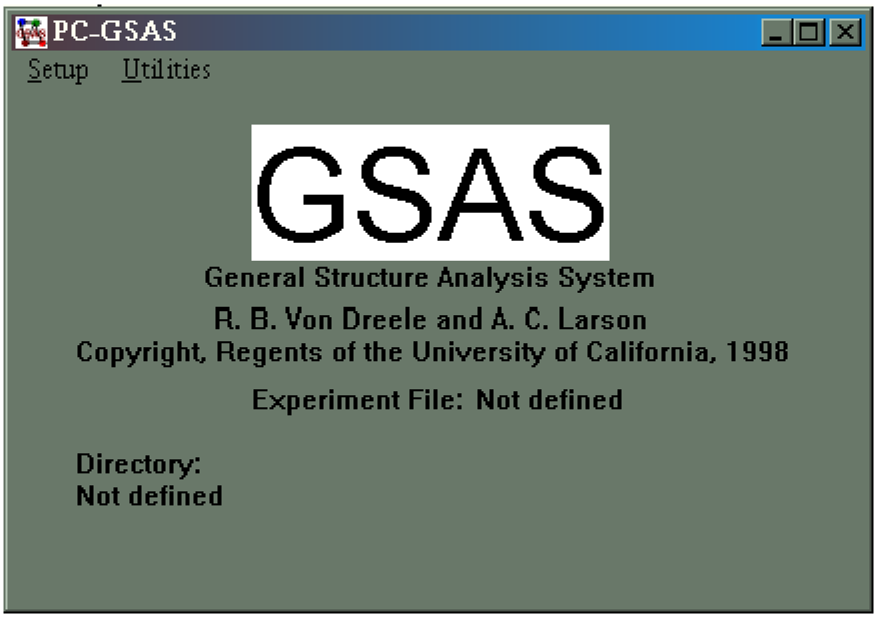
EXPEDT is the main program for entry of all controls, data and commands for the processing of diffraction data by GSAS. It is a multilayer menu driven interactive editor and is capable of monitoring input for crystallographic as well as typographical errors.

Starting GSAS

GSAS on a Unix machine is initialized by simply typing ëgsasí after the system prompt. The following opening screen for GSAS is then displayed on your workstation. Note: the pictured displays on your workstation may not exactly match those shown in this manual.

```
                    Welcome to GSAS
          The General Structure Analysis System


  Copyright, 1985-2000, The Regents of the University of California

Enter "help" for a listing of possible commands

No experiment name given
ltkiwi.lansce.lanl.gov GSAS Command:
```

The opening screen for the Windows95/98 version is obtained by clicking on the PC-GSAS shortcut; its appearance is different but conveys the same information.



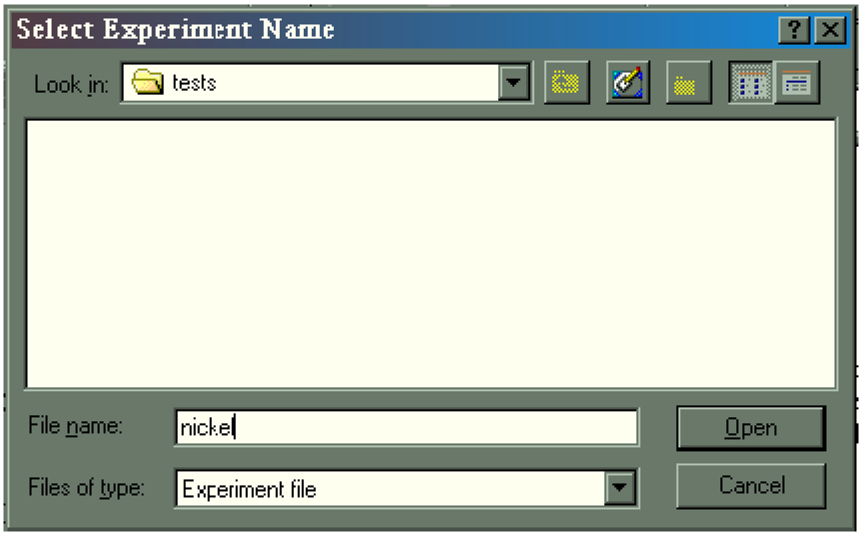
The message in the center of the screen results because GSAS fails to find an experiment file in your directory; the Unix version normally defines the first one alphabetically as the default experiment. Notice that the command line may also give the ìnode nameî for the particular computer you are working on. For Unix systems, type ëhelpí to display the main menu of components of GSAS.

```
The available GSAS commands are:
bijcalc    dbwscnv  forplot   gsas2pdb  polfplot  rawplot  scabs     vrstplot
cad4rd    disagl   forsrh    hklsort   powplot   rcalc    scmerge   x17bcnv
cconvstod dwtest   fourier   hstdmp    powpref   rducll   spcgroup
cllchg    expedt   genles    istats    proftest  ref2asc  sxtldata
convdtos   exptool  geometry  ortep     pubtable  ref2bin  tcldump
convstod   fitspec  gsas2cif  p3r3data  ramafit   reflist  unimol
utilities: atom next prev elst slst tlst dlst tlog dlog
           dexp texp lsexp pagelen convstod convdtos
"expnam" to set an experiment name
"quit" to leave GSAS & "help" for this help
No experiment name given
ltkiwi.lansce.lanl.gov GSAS Command:
```

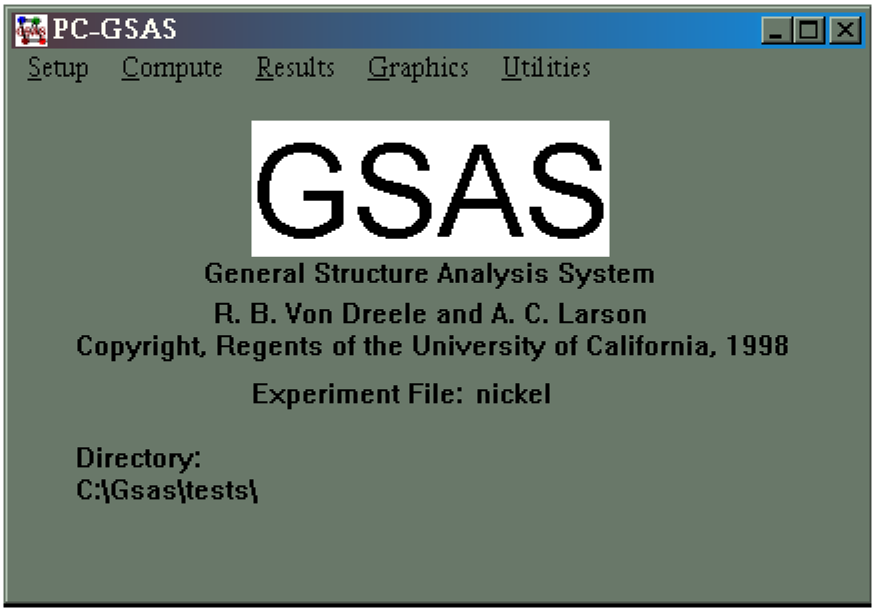
This listing includes general-purpose utilities (atom etc.) and all of the routines that are part of GSAS. All of the programs are started from this menu; notice that they all have lower case names. First you have to establish an experiment name for this training exercise; this name becomes the common file name for all files generated by GSAS programs. For Unix enter ëexpnam nickelí to set the experiment name. GSAS will then prompt for a new command.

```
**File not found: NICKEL.EXP
  The experiment is NICKEL
ltkiwi.lansce.lanl.gov GSAS Command:
```

For Windows 95/98 select the pull down menu ëSetupí and choose ëExpnamí; you will then see a file selection window.



Change directories until you have reached the desired location, enter ënickelí in the File name window and click on ëOpení. Answer ëYesí to the message; that will make the experiment name ënickelí. The main PC-GSAS window will then become



Notice that the pull down menus now have more choices and that the directory location is now defined (note: use of \gsas for working on problems is not recommended).

Running EXPEDT

For Unix the system warning message 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 ëexpedtí to initiate the program. For Windows 95/98 select ëSetupí and then ëExpedtí from the pull down menu; an MS-DOS window will be created. EXPEDT will display a question concerning your experiment.

```
Experiment - NICKEL - was not found in directory
C:\GSAS\TESTS
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 ëYí 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 either case simply type ë↵í, 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 66 character or less text string. 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 ëNickel Powder Data Inputí. 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 MS-DOS      |
                 | A menu driven routine to edit .EXP files |
                 | Distributed on 28/ 6/2000; 0:34:42       |
                 |------------------------------------------|

       |----------------------------------------------------------------|
       |           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, 2000, 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 ë↵í 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 ëPí. 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 ë?í 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 ëTí 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 ëPí.

```
There is no phase information present
*** No phase exists ***
Enter phase edit command(<?>,$,I,R) >
```

There are a few options; enter ë?í to see what they are.

```
Phase editing commands:
 <?> - Type this help listing
 $   - Enter DCL command
 I   - Insert new phase
 R   - Read phase info. from another experiment file
At least one phase must be defined before leaving this menu
*** No phase exists ***
Enter phase edit command(<?>,$,I,R) >
```

The ëRí option allows you to read phase information (name, lattice parameters, space group and atom positions) from another experiment file. This is useful when you are dealing with the same materials repetitively, for example in a quantitative phase analysis series. There is also the possibility of entering a system command with the ë$í command; one use may be to search a directory for the desired source of phase information. In this case we want to just enter a new phase so enter ëIí.

```
Enter identifying name for new phase number 1.
  >
```

Type a suitable name for this phase, i.e. ëNickel Powderí. 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 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 ëf m 3 mí for nickel; the character cases are converted by EXPEDT to conform to the standard, i.e. ìF m 3 mî. 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. Since nickel is cubic, only the "a" lattice parameter is requested. Type ë3.5234í; all the lattice parameters are displayed next.

```
Lattice parameters are
    a,b,c  =  3.523870  3.523870  3.523870
    angles =    90.000    90.000    90.000
    volume =    43.758
Lattice symmetry is cubic
Space group symmetry is cubic
Enter phase edit command(<?>,$,D,E,F,M,I,L,R,S,X) >
```

After one phase has been entered you now have the opportunity for further phase editing commands. Enter ë↵í or ë?í 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 - Modify phase type flag for phase "n"
 L   - List phase names
 R   - Read phase info. from another experiment file
 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,R,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 ëIí command; the same sequence of questions as above will then appear. The ëMí option is used to change the type of phase. Available types are: ìchemicalî structure (i.e. no magnetism and less than 500 atoms; this is the default), mixed magnetic and chemical structure, pure magnetic structure and macromolecular (i.e. more than 500 atoms) structure. You have only one phase in this sample and it has been entered so type ëXí.

```
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 ë↵í 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 ëHí 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 ë↵í 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 ëIí.

```
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 ë↵í.

```
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 DOS (or Unix) command to locate it. In this case the file

/gsas/example/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 ë/gsas/example/NICKEL.RAWí for either Unix or MS-DOS/Windows versions of GSAS.

```
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 first record from the file and asks if it is the correct one. If you answer ëNí, it will ask for another data file name; the ëQí option is used to exit from EXPEDT. This title is taken from one of the records in /gsas/example/NICKEL.RAW and originated from a title given when the data was collected. Since this is the correct data set type ë↵í.

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

You are now requested to enter the name of a file that contains instrument specific information. Type ë↵í to see the help listing.

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

Again you can enter DOS (or Unix) commands to help locate the proper file name. The proper filename for this exercise is ë/gsas/example/inst_tof.prmí. Enter this name.

```
The raw data file is : /gsas/example/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 ëbanksí of detectors. To see the characteristic 2Θ values for each of the banks type ë-1í.

```
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/example/nickel.raw

Enter bank number desired (<0 for list, 0 to quit) >
```

You will use banks 2 and 3 for this exercise, so type ë2í to read the data from the ~90 bank. There will be a short 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 ëYí, 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 ë↵í.

```
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,M,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 ë↵í or ë?í 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
 M   - Modify incident spectrum source
 P   - Plot histogram
 S   - Edit the data sampling factor
 T   - Set max 2-Theta or Energy or min TOF (equivalent to D option)
 W   - Edit profile params.
Enter histogram data modification command (<?>,A,B,C,D,E,F,I,L,M,P,S,T,W) >
```

Notice that this menu has no exit (ëXí) command; this is because the minimum d-spacing must be set first by either the ëDí or ëTí options. However, it is helpful to display the powder pattern before setting the minimum d-spacing. Type ëPí to display this histogram.

```
Enter graphic screen option (<?>,A,B,Z) >
```

This version of this menu will appear on the MS-DOS/Windows version of GSAS; the one for Linux has an additional option ëCí. You must now select the proper choice for your graphics display; type ë?’ to see the list of supported graphics resolutions.

```
Graphics screen option:
 A    Low resolution (640x480)
 B    Medium resolution (800x600)
 Z    No screen graphics; only hardcopy
Enter graphic screen option (<?>,A,B,Z) >
```

Choose the appropriate code for your terminal; option ëAí will always work in any version of Windows. The ëBí option sometimes fails for lack of a proper graphics driver. Option ëZí is used when EXPEDT is part of a batch process and no screen graphics is desirable. If you are working on Unix workstation then the choices are for persistent and non-persistent X-windows graphics or an ìold fashionedî Tektronix graphics terminal. You will immediately see the next option.

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

If you respond ëY’ to this question then the following menu appears. In the present case type ë↵í and the next two listings will not be seen.

```
Enter hardcopy option (<?>,A,B,C,D,E) >
```

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

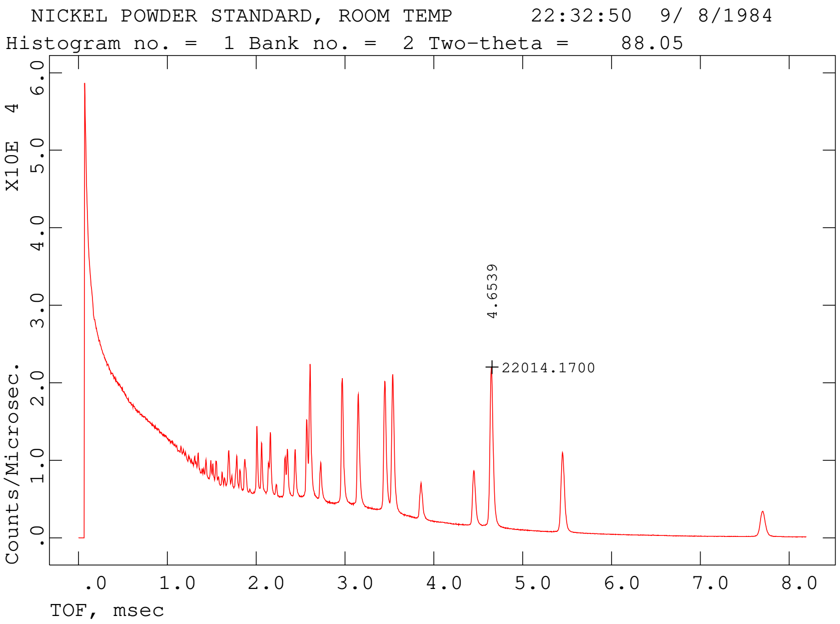
```
High resolution hardcopy device:
 A    HP Laserjet printer
 B    PostScript printer
 C    EPS PostScript file
 D    Color PostScript printer
 E    Color EPS PostScript file
Enter hardcopy option (<?>,A,B,C,D,E) >
```

For the selected hardcopy device, the system produces a file named "experiment.device" with the appropriate graphics codes. To obtain the hardcopy, the file must be sent to the appropriate device; this may be attached to your computer or be a network device. 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 EPS plots are each saved to separate files with only one plot per file; in this case the file name is requested of the user for each saved plot.

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 ëYí to this question and EXPEDT will subsequently ask for a range in TOF (or 2Θ, as appropriate) for the first plot. As this is the last chance before the graphics is displayed, you should be sure the display is in full MS-DOS screen mode and not Window mode. On some PCís attempting to do DOS graphics in a Window will cause the program to fail or even crash the machine! Enter ëAlt-↵í to toggle between modes. Since you probably haven't seen this data before, type ë↵í and the full pattern will be displayed as the first plot.



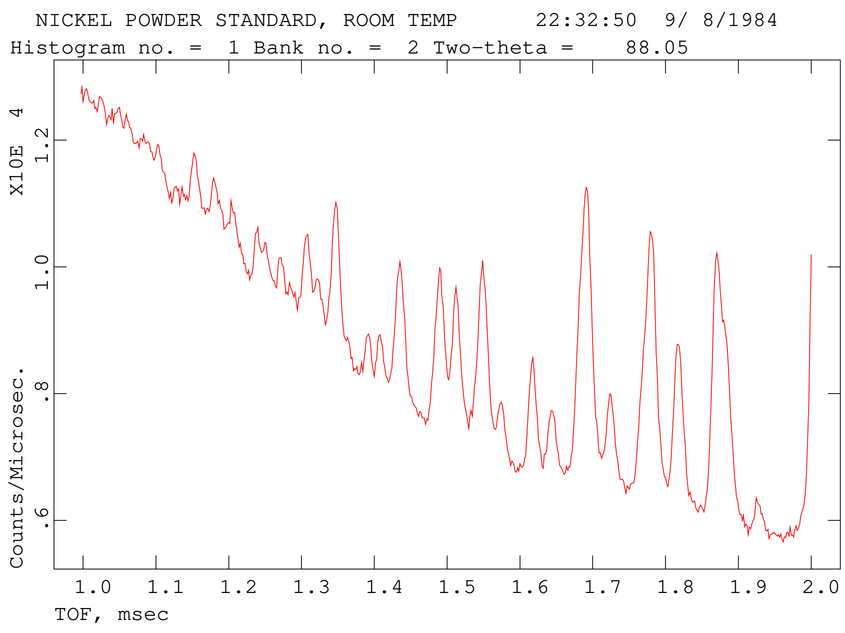
After the plot is finished a graphics cursor will appear. The commands for using this cursor are given at the bottom of the plot; it can be used to find the position and height of a feature in the pattern. For an X-Windows workstation the attached mouse is used to position the cursor and the buttons are active; an additional help message indicates their use. The two figures near the peak at ~4.5 msec were obtained by typing ëWí and ëHí after positioning the cursor at the peak top. No return (ë↵í) is needed for most terminals; you should wait for the cursor to appear before entering a subsequent cursor command. Enter ëXí (remember no ë↵í) to exit the cursor mode. 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. Type ë↵í to continue; the graphics will vanish and the following line will next appear:

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

The appropriate response here is to give two values covering some part of the full range of the initial plot, entering ë0 0í will give the full range. In this case you want to look at the shortest TOF part of powder pattern containing Bragg peaks (1-2 msec) so type ë1 2í. 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 ëSí. If you respond with ëRí, EXPEDT will then request new values for Y-minimum and Y-maximum. You want the plot to be automatically rescaled so type ëAí. The new plot will then be drawn and should look like:



Again a graphics cursor appears, enter ëXí (no ë↵í) to exit the cursor mode. Note that the lowest TOF where there are still Bragg peaks is about 1.1msec; this value will be needed shortly. Type ë↵í to continue; again the plot will vanish and 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 ë↵í. The following menu will appear.

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

Now you want to set the minimum d-spacing by setting the minimum TOF. Type ëTí to select this option.

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

As you could 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. Enter ë1.1í 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,M,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 ëCí.

```
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 ë2í.

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

You are finished editing this histogram so type ëXí; 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/example/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 ë3í, again there will be a short 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>)? >
```

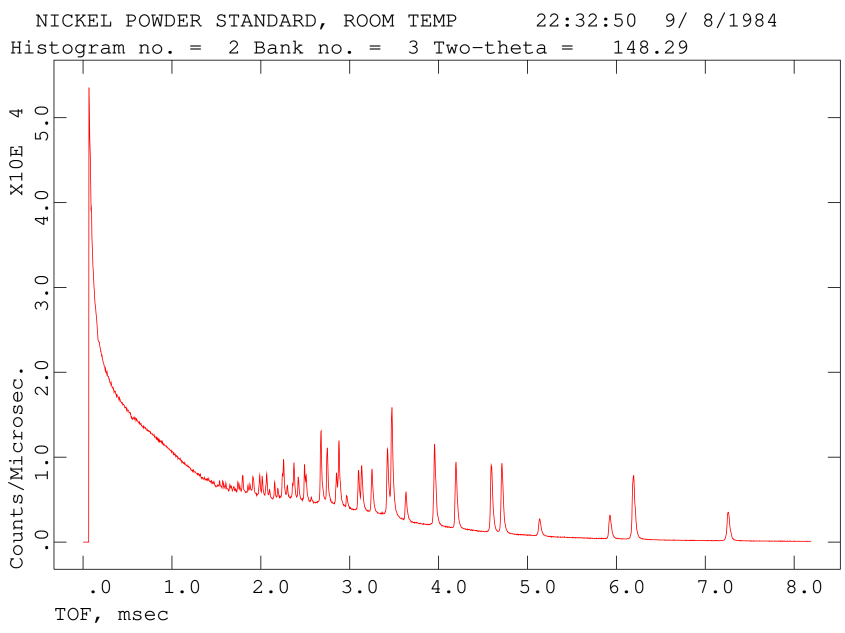
As with the first histogram you can preview the histogram before letting GSAS use it; but the data is OK so type ë↵í.

```
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,M,P,S,T,W) >
```

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

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

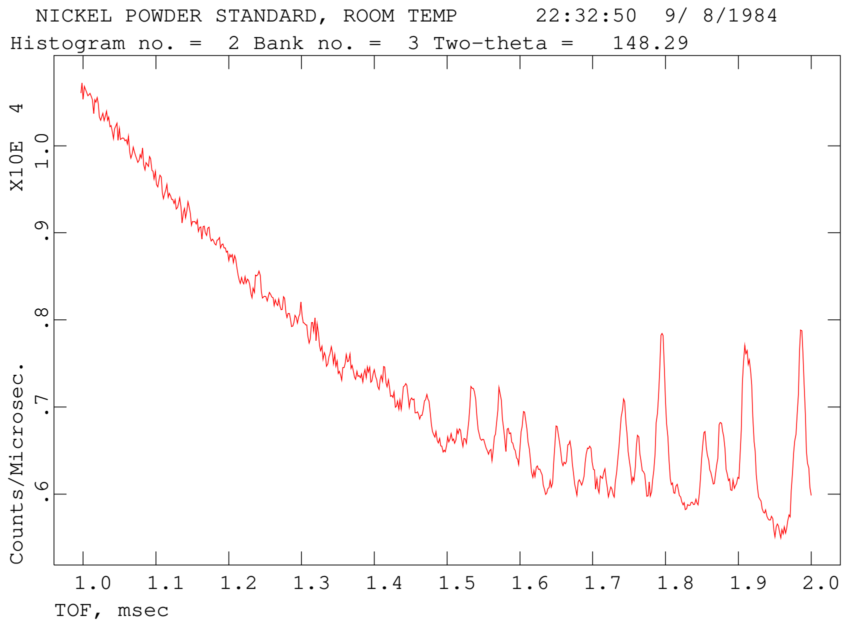
Again you don't know what to expect for this pattern, so type ë↵í. Since the terminal type is already known to EXPEDT, the plot appears immediately.



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 ëXí and ë↵í 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 ë1   2   a'.



Note that Bragg peaks begin to appear just above 1.5msec; this value will be needed shortly. Again type ëXí and ë↵í 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 ë↵í to continue. The menu for editing histogram data will be displayed.

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

Select ëTí 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 ë1.5í 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 ë/í to accept it; the following will be 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,M,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 ëWí 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 ëWí.

```
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) =    .0000 N #3(bet-0) =   5.5766E-02 N #5(sig-0) =       .000 N
#2(alp-1) =    .1374 N #4(bet-1) =   1.3723E-03 N #6(sig-1) =     48.764 N
#8(rstr ) =     .000 N #9(rsta ) =         .000 N #7(sig-2) =       .000 N
#10(rsca) =     .000 N #11(s1ec) =          .00 N #12(s2ec) =        .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 ë?í 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 ëW 0.5í. 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 ëXí.

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

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

```
The raw data file is : /gsas/example/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 ë0í. 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 (<?>,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 ë?í to see the full help listing.

```
Histogram modification options:
 <?> - Type this help listing
 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 - Toggle use of 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 (<?>,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 ëUí option is used to mark histograms so that they will not be used by GENLES. These instructions are only effective on powder data histograms after first processing them with POWPREF. You are finished with histogram editing so type ëXí.

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

You are done with editing of powder data so type ëXí. 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 ë?í 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 ëXí and EXPEDT will terminate.

```
EXPEDT terminated successfully
```

For GSAS in Windows, the MS-DOS Window that was running EXPEDT will have a title indicating ëFinished- EXPEDTí. Close this window by clicking on the small ëxí in the upper right corner of the Window frame. In Linux the main GSAS prompt will appear with NICKEL identified as the experiment name.

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. For Unix you start with the main GSAS prompt; type ëpowprefí to initiate the program. For Windows 95/98 select ëComputeí and then ëPowprefí from the pull down menu; an MS-DOS window will be created. Processing will immediately start as POWPREF has no interactive capability.

```
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
```

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. In MS-DOS/Windows an error will be produced if one attempts to run any GSAS routine that tries to open an experiment file that is currently opened by some other GSAS routine. POWPREF will open a listing file ëNICKEL.LSTí 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. For Unix the GSAS utility ëDLSTí can be used to delete this file. When POWPREF completes you can print NICKEL.LST or examine it on your terminal with the Unix GSAS utilities ëELSTí or ëTLSTí. For Windows this file can be examined with any simple text editor; the ëPfeí editor by Alan Phillips is especially useful. 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 the POWPREF run 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

In Unix POWPLOT is run from the GSAS command level by entering ëpowplotí after the prompt. For Windows select ëPowplotí from the ëGraphicsí pull down menu. The program will display a copyright message and prompt for a letter identifying the kind of terminal you are working on.

```
                      |------------------------------------------|
                      |      Program POWPLOT Version MS-DOS      |
                      |      Powder pattern plotting program     |
                      | Distributed on 28/ 6/2000; 0:37:26       |
                      |------------------------------------------|

         |----------------------------------------------------------------|
         |            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, 2000, The Regents of the University of California.  |
         |----------------------------------------------------------------|

The last history record is :
    HSTRY  2 POWPREF MS-DOS 2000-07-07T09:56:51

Enter graphic screen option (<?>,A,B,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 ëYí. We will assume that you entered ëNí. 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 ë?í or ë↵í to obtain the full help listing.

```
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 ëLí to see the list of histogram titles and the current state of all the toggles.

```
The last history record is :
    HSTRY  2 POWPREF MS-DOS 2000-07-07T09:56:51

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 ëH 1í or ëNí to read it. There will be a short pause as the file ëNICKEL.P01í is read.

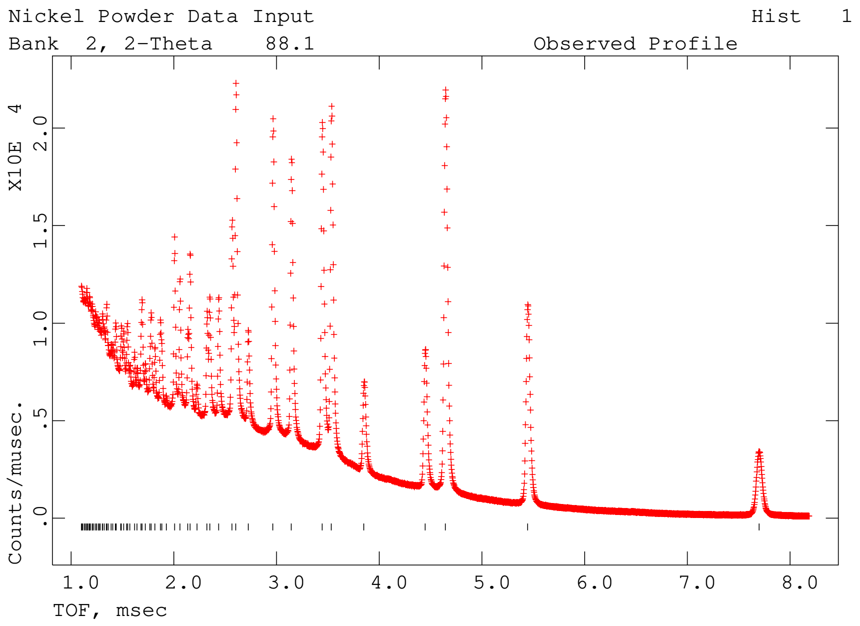
```
The selected histogram is:
Histogram no.   1 Bank no.  2 Two-theta =    88.05
Title:   NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
**** Histogram will be used in least-squares
Reading histogram - please wait
Enter command (<?>,B,C,D,H,I,L,M,N,O,P,R,S,T,X) >
```

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 that 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 ëM Tí. 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 ëPí to cause the plot to be drawn on the screen. Assuming that your toggles are set the same way, it should look like this:

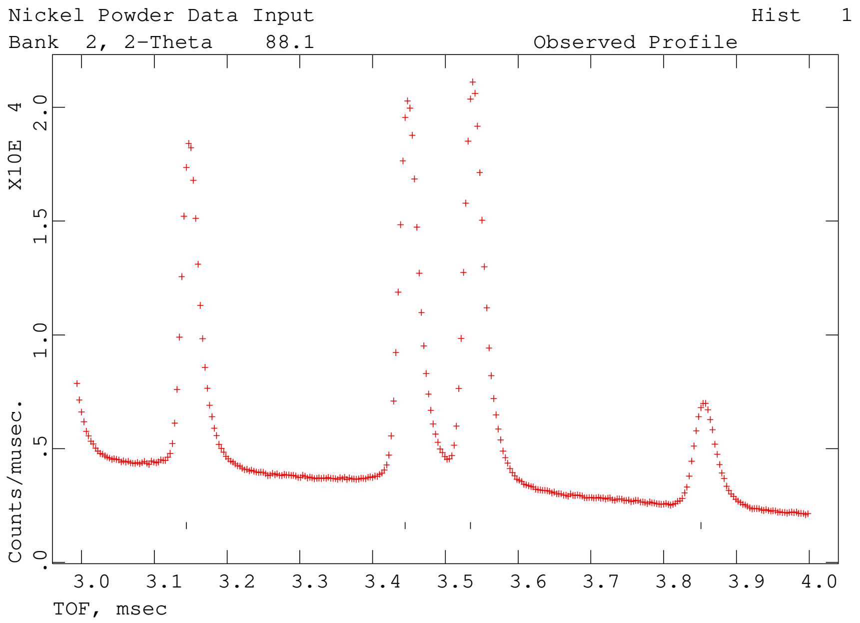


Notice that the reflection markers closely correspond to the peak positions. If the lattice parameters or diffractometer zero point had incorrect values the markers would not lie under the peak positions. This situation would probably cause GENLES to fail or at best converge very slowly. You would have to correct the values with EXPEDT and rerun POWPREF before continuing. You may have to type ë↵í 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 ëSí 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 ë3 4 Aí. The new plot will then be drawn and should look like:



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 ë↵í 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) >
```

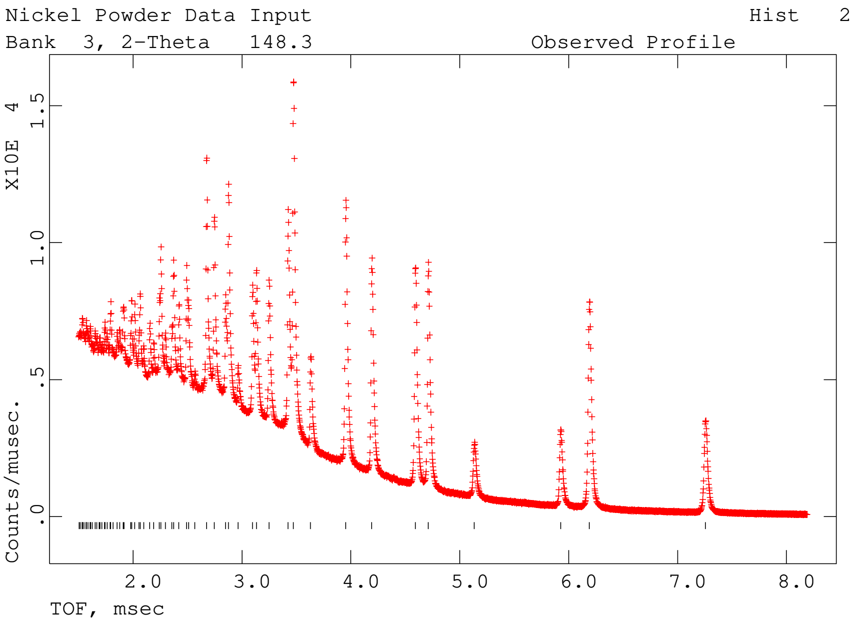
Respond this time with ë↵í.

```
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 ëNí; the title and status of the second histogram will be displayed. Again there is a short pause while ëNICKEL.P02í 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) >
```

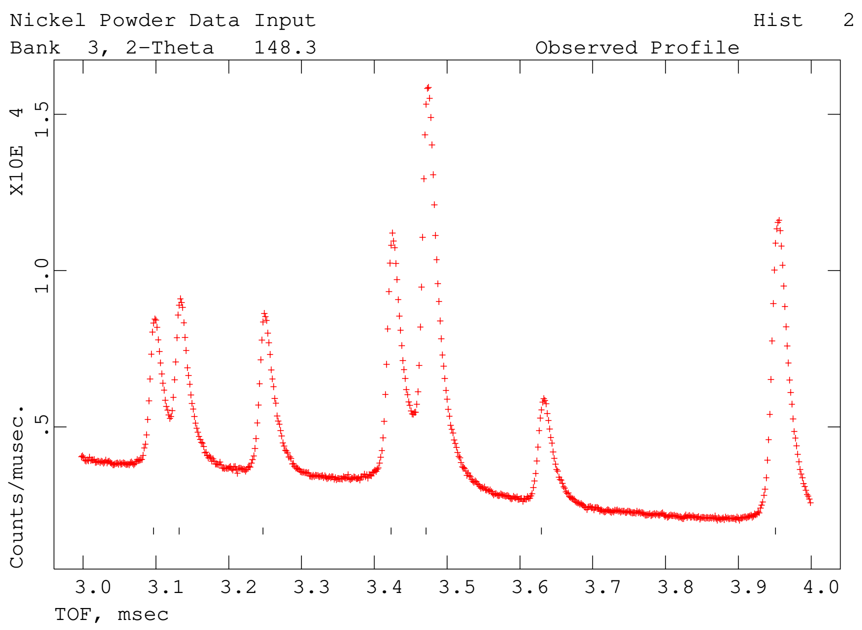
The set of toggles used for the first histogram are still in force; you want to plot this histogram so type ëPí. The plot will immediately follow.



As before the blinking cursor indicates the plot is finished; type ë↵í 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 ë3 4 Aí. 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 ë↵í if needed to continue.

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

Respond with ë↵í.

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

You are all done so type ëXí; POWPLOT will terminate.

```
POWPLOT terminated successfully
```

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 Unix GSAS command level by typing ëexpedtí; the experiment name ëNICKEL' must have previously been selected with the ëexpnam' command. For Windows select ëSetupí and then ëExpedtí from the pull down menu. The copyright message will be displayed followed by a summary of your last operation on this experiment and a menu.

```
                    |-------------------------------------------|
                    |        Program EXPEDT Version MS-DOS      |
                    | A menu driven routine to edit .EXP files  |
                    | Distributed on 28/ 6/2000; 0:34:42        |
                    |-------------------------------------------|

          |-----------------------------------------------------------------|
          |            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, 2000, The Regents of the University of California.  |
          |-----------------------------------------------------------------|

The last history record is :
    HSTRY  2 POWPREF MS-DOS 2000-07-07T09:56:51

Is this the file you wish to use? (<?>,K,Q,R,Y) >
```

The ëhistory recordí 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 ë?í to see your options.

```
The options here are:
 K - Live dangerously. NO NEW COPY, NO BACKUP!
 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? (<?>,K,Q,R,Y) >
```

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 ëKí 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 ëYí. A new copy of ëNICKEL.EXPí is created and the previous version is renamed ëNICKEL.OLDí.

```
Experiment title:
         Nickel Powder Data Input
The last history record is :
    HSTRY  2 POWPREF MS-DOS 2000-07-07T09:56:51

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

The experiment title is the one entered in your first session with EXPEDT. To see the help listing, type ë?í or just ë↵í.

```
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) >
```

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 ëLí.

```
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. Enter ë?í 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 ëTí.

```
Enter title editing command (<?>,L,T,X) >
```

Enter ë?í to see what these choices are.

```
Experiment title editing menu
  L - List current title
  T - Experiment title
  X - Exit from this menu
Enter title editing command (<?>,L,T,X) >
```

The option you want is ëTí; enter that.

```
Old Experiment title
Nickel Powder Data Input
Enter new Experiment title(/ for no change) >
```

So that the next set of titles reflect the status of the nickel problem enter ëNickel Powder Refinementí.

```
Enter title editing command (<?>,L,T,X) >
```

Now enter ëXí to return to the main least squares menu.

```
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 ëAí.

```
Phase No. 1; Phase has      0 atoms; 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 ë?í 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; Phase has      0 atoms; 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 ëI 1í. You are then prompted for some information about atom ë1í.

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

You are prompted to enter the atom ëTYPEí 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 ëNI+2_58í (note the underscore ë_í) would load the Ni^{2+} x-ray and the ^{58}Ni neutron scattering data. Specifying a TYPE of just ëNI' 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 ìnatural abundanceî 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 ëFRACí 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 ëNI 0 0 0 1í.

```
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 cannot contain imbedded blanks or commas. You assume that this one is OK so type ë/í.

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

The ëFLAGí requested is to tell EXPEDT whether you are going to enter an ëIísotropic temperature factor, U_{iso}, or a set of six ëAínisotropic 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 ëI 0.004í. 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    .00000  .00000  .00000 1.00000 NI1       .00400 I       M3M    4 000
Phase No. 1; Phase has      1 atoms; 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 ëIí in the column marked ëCODEí; these are places for atom refinement codes. Later you can refine atom parameters and the codes ëFí, ëXí, ëUí 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 ëSTSYMí and ëMULTí give the point symmetry and the number of equivalent positions in the cell for this atom location. The last column marked ëFXUí 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 ë↵í 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; Phase has      1 atoms; 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 ë?í 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 ëI Ní. Alternatively you can choose a sequence number by entering ëI ní, where ëní is an integer in the range 1-999 that has not been used before. 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 ëCí).

You have successfully entered the required nickel atom so type ëXí 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 ëLí.

```
Maximum number of cycles is   3
Enter L-S control editing option (<?>,A,B,C,D,E,J,L,P,V,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 ë?í to see the help listing.

```
 A a - Maximum atom position shift
 B b - Matrix band width (0 full matrix)
 C n - Maximum number of cycles
 D d - Marquardt factor
 E   - Change powder data Fobs extraction flags
 L   - List current settings
 P   - Select options for the output listing
 V n - Convergence criterion
 X   - Exit from editing least squares controls
Enter L-S control editing option (<?>,A,B,C,D,E,J,L,P,V,X) >
```

The ëEí 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 reflection intensities. These calculated values are either obtained using the atom parameters or derived by the LeBail procedure, where the calculated intensities are obtained from the set of observed values extracted in the previous refinement cycle. These extracted intensities are converted to structure factors (F_o^2) and saved on the ëexpnam.Rnní file. The ëPí option allows you to request additional information beyond the default to be printed in the GENLES list output. You are done here so type ëXí 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 ëOí.

```
Enter overall parameter to be edited (<?>,A,B,C,D,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 ë?í to see the help listing.

```
Overall parameters editing options:
 <?>  - Type this help listing
 A   - Absorption coefficients
 B   - Background coefficients
 C   - Diffractometer constants
 D   - Diffuse scattering parameters
 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,D,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 ëINSTPARM.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 ëBí 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)
    .100000E+01    .000000E+00    .000000E+00    .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 ëRefinement flagí equals ëYí; 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 function selected by default (#4) is usually appropriate for neutron TOF data. 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 ë?í to see the help listing.

```
Background edit commands:
 <?> - Type this help listing
 B   - Modify the full background refinement flag
 C   - Change background function type, number of 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   - List 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, ëHí and ëNí. The latter one is most convenient because it simply steps to the next histogram. Since everything is satisfactory for the first histogram, type ëNí 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)
    .100000E+01    .000000E+00    .000000E+00    .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 ëXí to return to the overall parameter editing menu.

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

You now want to examine the scale factors for the two histograms so type ëHí.

```
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 ë?í 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 satisfactory, step to the second by typing ëNí.

```
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 satisfactory so type ëXí to return back to the overall parameter menu.

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

There are no other overall parameters that need to be examined at this time so type ëXí 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 ëXí to return to the main EXPEDT menu.

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

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

```
EXPEDT terminated successfully
```

Refinement of Powder Data - Program GENLES

The next step is to run GENLES and refine the selected parameters for the ëNICKELí problem, namely the two scale factors and eight background parameters. In Unix, GENLES is run by entering ëgenles' after the GSAS prompt. For Windows select ëGenlesí under the ëComputeí pull down menu; an MS-DOS window immediately opens. As GENLES is usually the longest running program within the GSAS suite, its progress is given by a brief summary of statistical information for each cycle of refinement. In this case the calculations are very quick. Three cycles of refinement suffice to obtain convergence.

```
Restraint data statistics:

Powder data statistics                Fitted        -Bknd            Average
             Bank Ndata Sum(w*d**2)  wRp     Rp    wRp     Rp     DWd  Integral
Hstgm  1 PNT   2  2215  40694.      .0409  .0314  .0390  .0298    .176     .988
Hstgm  2 PNT   3  4182  20381.      .0346  .0261  .0360  .0266    .244     .997
Powder totals     6397  61076.      .0384  .0293  .0379  .0286    .199
Cycle   3 There were  6397 observations. Total before-cycle CHI**2 = 6.1075E+04

Reduced CHI**2 =  9.562     for    10 variables
Histogram  1  Type PNT   Nobs=  105 R(F**2) =   .1972
Histogram  2  Type PNT   Nobs=   97 R(F**2) =   .1178

Final variable sum((shift/esd)**2) for cycle   3:        .00 Time:     .94 sec

Convergence was achieved and
GENLES terminated successfully
```

The displayed output from the last least squares cycle are shown above. The item under ìRestraint data statistics:î is empty since no restraints were used in this refinement. The next block shows results from fitting the two powder histograms and following that are the residuals from comparison of the calculated F_c^2 structure factors and those F_o^2 structure factors extracted from the profile during the Rietveld refinement. Finally, the running time is given for that cycle and convergence is noted.

For Unix, GENLES simply runs in the terminal window that had the GSAS prompt. The screen output will be the same as given above for Windows.

The running time for this job will be a few seconds to 5 minutes depending on your system. As with POWPREF, wait for GENLES to finish before continuing on with the training exercise. GENLES will append its output to the listing file ëNICKEL.LSTí 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 Unix GSAS utilities ELST or TLST or any Windows text editor. This listing is 128 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

For Unix run POWPLOT from the GSAS command level by typing ëpowplotí; for Windows select ëPowplotí from the ëGraphicsí pull down menu. The program will display a copyright message and prompt for a letter identifying the kind of terminal you are working on.

```
                   |------------------------------------------|
                   |      Program POWPLOT Version MS-DOS      |
                   |      Powder pattern plotting program     |
                   | Distributed on 28/ 6/2000; 0:37:26       |
                   |------------------------------------------|

        |---------------------------------------------------------------|
        |           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, 2000, The Regents of the University of California. |
        |---------------------------------------------------------------|

The last history record is :
    HSTRY  4 GENLES  MS-DOS 2000-07-07T12:21:11  Sdsq=  .611E+05 S/E=  .335E-04

Enter graphic screen option (<?>,A,B,Z) >
```

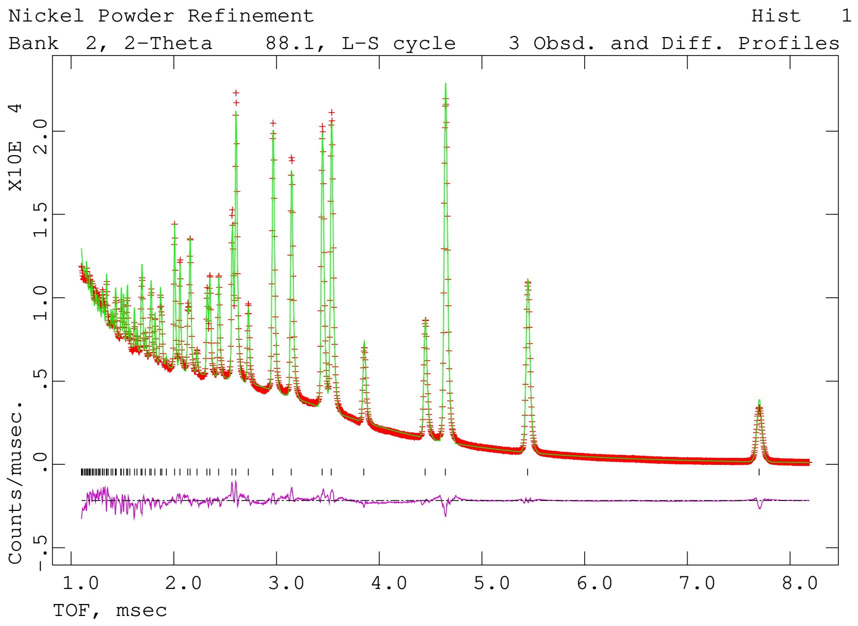
Enter the letter that describes your terminal and then respond ëNí to the hardcopy question. The main menu will be displayed.

```
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 ëNí or ‘H 1í.

```
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) >
```

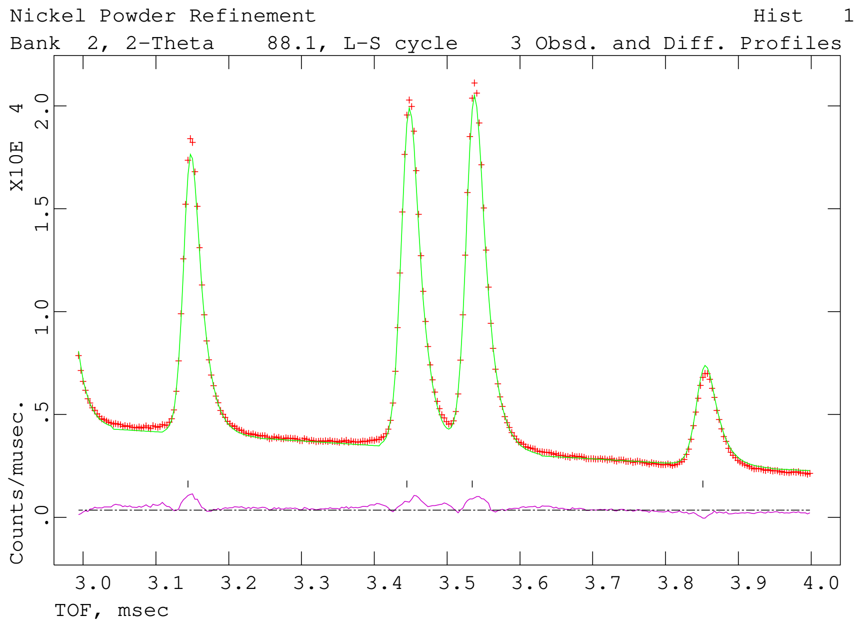
You want to plot the first histogram, display the reflection markers and show the difference curve. You also want the X-axis to show TOF. All of the relevant commands can be entered on one line so type ëM D T Pí. Spaces or commas must separate each entry. Immediately before the plot appears, a few lines may 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 are 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 ë↵í if needed to continue; the following line will appear:

```
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 ë3 4 Aí. 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 ë↵í 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 ë↵í.

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

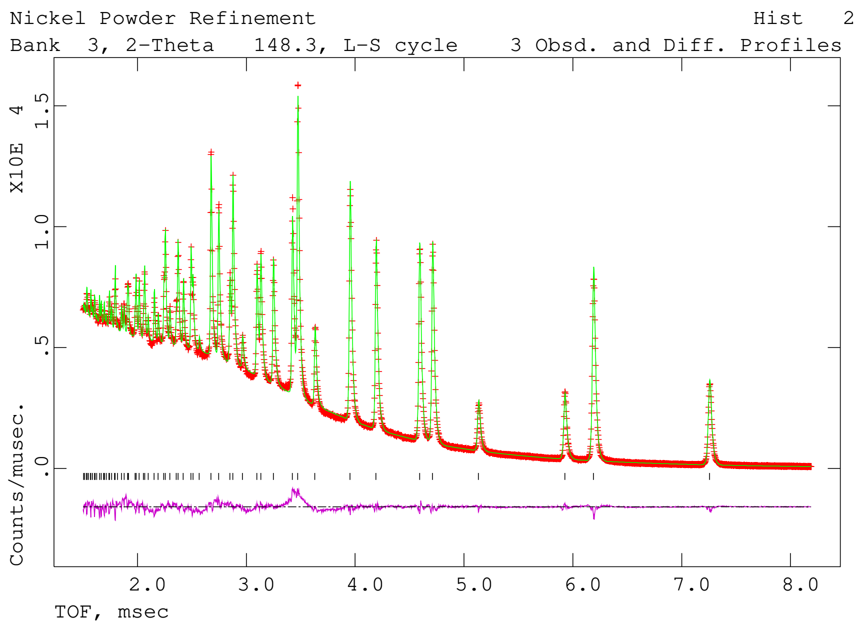
If there is a set of calculated values for the histogram, you have the option of viewing a series of graphs that depict the distribution of differences (I_O-I_C) with, in this case, TOF and compare them with a normal distribution. This is normally only useful when the fit is very close so respond ëNí 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 ëH 2í or ‘Ní; 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) >
```

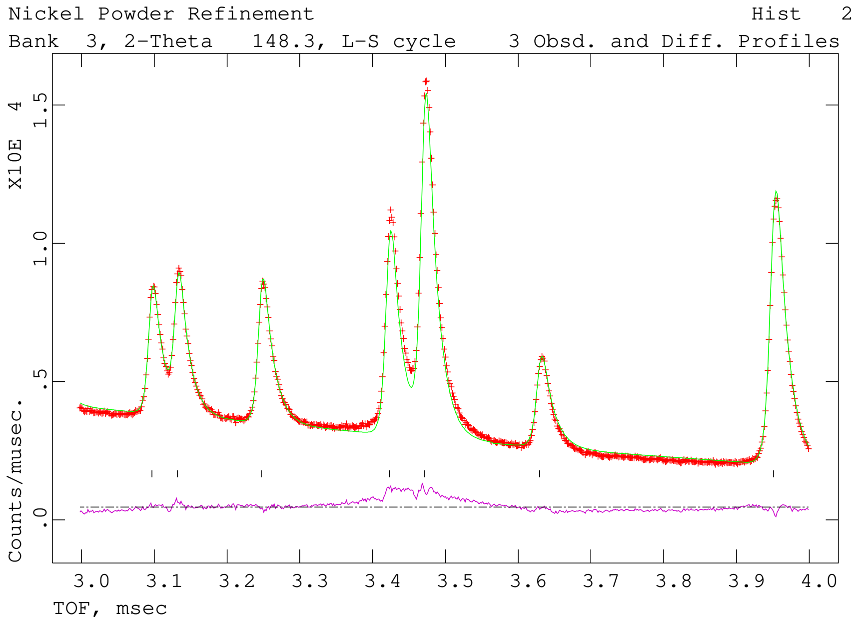
The same set of toggles used for the first histogram are still in force; to plot this histogram type ëPí. The plot will immediately follow.



In this case the overall fit is much better and the difference curve is much flatter. Enter ë↵í if needed to continue. The following line will appear:

```
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 ë3 4 Aí. The new plot will then be drawn and should look like:



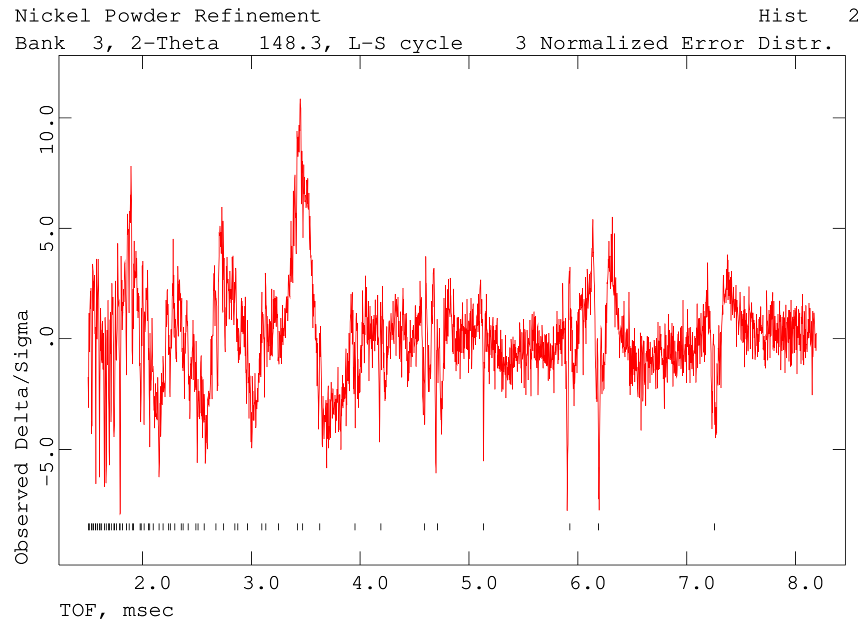
The major feature in this difference curve is a broad peak at ~3.45 msec; this is the (111) reflection offset by one TOF frame. Type ë↵í if needed to continue.

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

Respond with ë↵í.

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

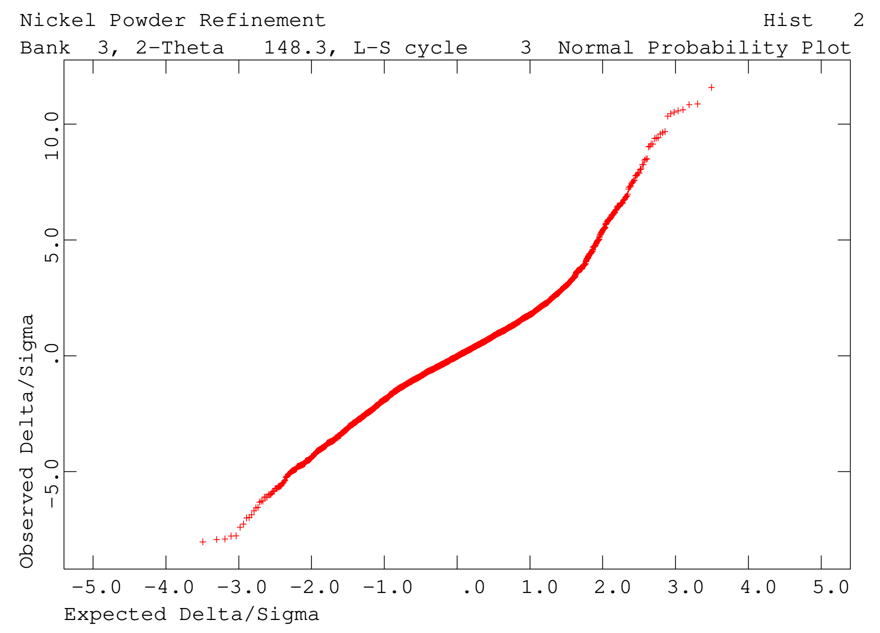
In this case the fit is very good and it is worthwhile doing the error analysis. Type ëYí, the plot of $(I_o-I_c)/\sigma(I_o)$ verses TOF will immediately follow.



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. Type ë↵í 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 ë↵í. The next plot is the ìnormal probability plotî 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 ë↵í 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 ë↵í 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 ë/í.

```
The slope & intercept of the normal probability plot are    1.9896    -.0146
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.

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

You are all done so type ëXí; POWPLOT will terminate.

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 ëexpedt’ at the GSAS prompt or else select it from the ëSetupí pull down menu as appropriate. After the copyright message there will be a history record displayed.

```
                 |-------------------------------------------|
                 |        Program EXPEDT Version MS-DOS      |
                 | A menu driven routine to edit .EXP files |
                 | Distributed on 28/ 6/2000; 0:34:42        |
                 |-------------------------------------------|

       |---------------------------------------------------------------|
       |            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, 2000, The Regents of the University of California. |
       |---------------------------------------------------------------|

The last history record is :
    HSTRY  4 GENLES  MS-DOS 2000-07-07T12:21:11  Sdsq=  .611E+05 S/E=  .335E-04

Is this the file you wish to use? (<?>,D,K,Q,R,Y) >
```

GENLES creates a new version of the experiment file that 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 ëYí; 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  MS-DOS 2000-07-07T12:21:11  Sdsq=  .611E+05 S/E=  .335E-04

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

Since you are continuing on with more least squares refinement, type ëLí 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 ë?í response to see the help listing if you get lost. As a last resort the exit from any menu is ëXí. If you make a mess of your experiment file, the ëQí 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 ëCí 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 ësigí parameters first; they are profile coefficients 5-7. Don't forget that there is a set for each histogram.

Other parameters

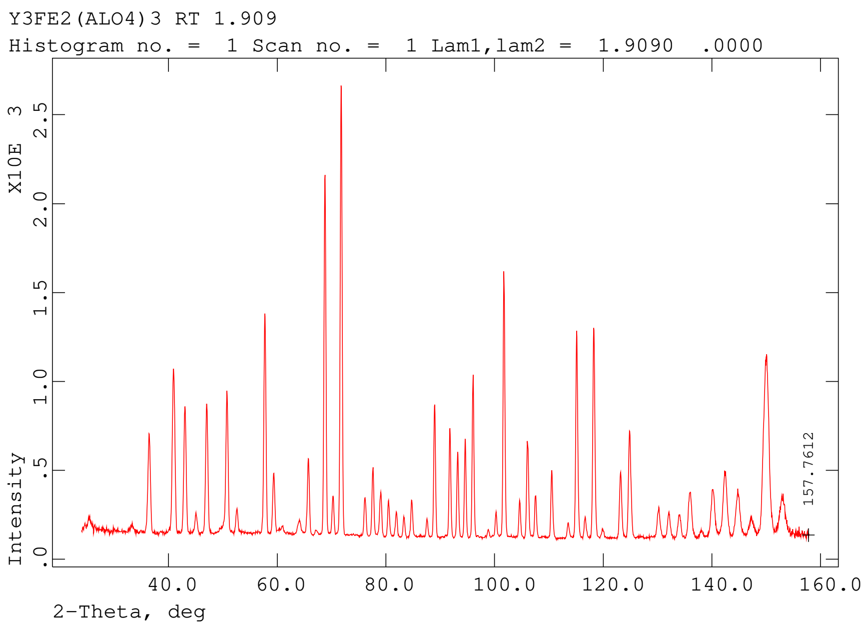
The other parameters that may be refined for the nickel example include the absorption and extinction factors and the lattice parameters. We encourage you to try all of these parameters to get a feel for the sensitivity of the refinement to each of them as well as see how they are edited with EXPEDT

Neutron CW Powder Data - 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 1.909 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 (ëGARNETí would be a suitable name) type ëexpedtí to start data preparation. Again the powder data preparation option ëPí is used to introduce new data to the system. The space group for this garnet is ëI a 3 dí and the cubic lattice parameter is ca. ë12.19í. 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 ëF Cí for inserting the chemical formula from the phase editing menu. The raw data can be found in the file ë/gsas/example/GARNET.RAWí and the instrument file is ë/gsas/example/INST_D1A.PRMí. There is only one histogram corresponding to a scan from 20° to nearly 160° 2Θ. The scan number for this histogram is ë1í and the corresponding instrument parameter set is also ë1í. 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 ëTí option and give a maximum 2Θ of ë159í that 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 ëLí 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     .12500  .00000  .25000 1.00000 Y1        .01000 I    222(100) 24 000
  2 FE    .00000  .00000  .00000  .60000 FE2       .01000 I     -3(111) 16 000
  3 AL    .00000  .00000  .00000  .40000 AL3       .01000 I     -3(111) 16 000
  4 AL    .37500  .00000  .25000  .75000 AL4       .01000 I     -4(100) 24 000
  5 FE    .37500  .00000  .25000  .25000 FE5       .01000 I     -4(100) 24 000
  6 O   -.03000  .05000  .15000 1.00000 O6        .01000 I         1    96 000
```

This listing is obtained by entering ëLí 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 ëKí 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 ëI' to insert the first one.

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

Enter ë1 UISO 2 1í for the first term and ë1 UISO 3 1í for the second. Then enter ë↵í 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 ëIí for the first one.

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

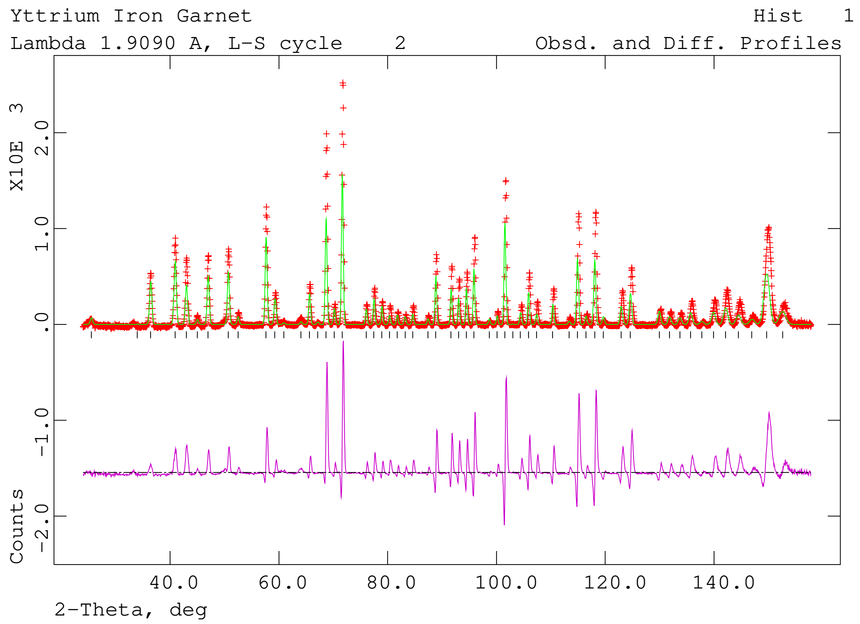
Enter ë1   FRAC   2   1í followed by ë1   FRAC   3   -1í and a ë↵í for the first FRAC constraint. This means that FRAC for atom 3 will decrease if FRAC for atom 2 increases and visa-versa. In a similar fashion enter a constraint on FRAC for atoms 4 and 5; remember to change the sign of the coefficient for the second term. When you are done there should be four constraints for the two pairs of atoms. Enter ëLí 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 ëX   X   Xí to return to the main EXPEDT menu. You may now exit from EXPEDT by entering ëXí.

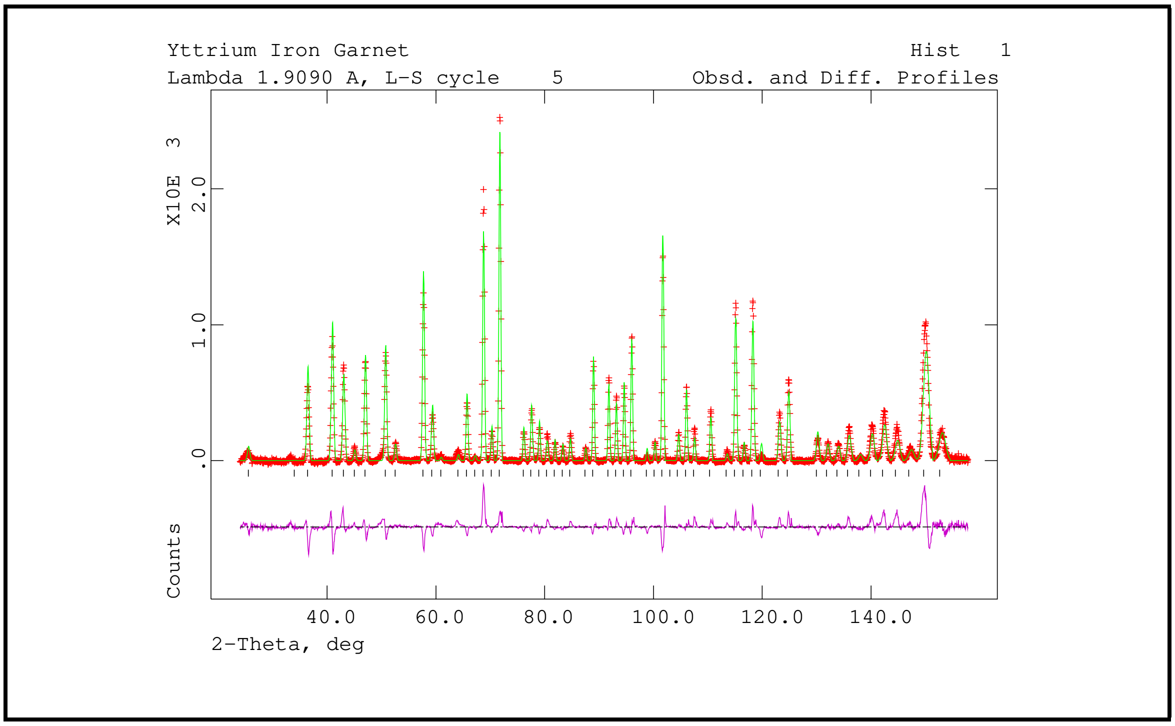
Powder Data Preparation and Refinement

You are now ready to run the two calculations, POWPREF and GENLES. After both jobs finish use POWPLOT to look at the results of the refinement.



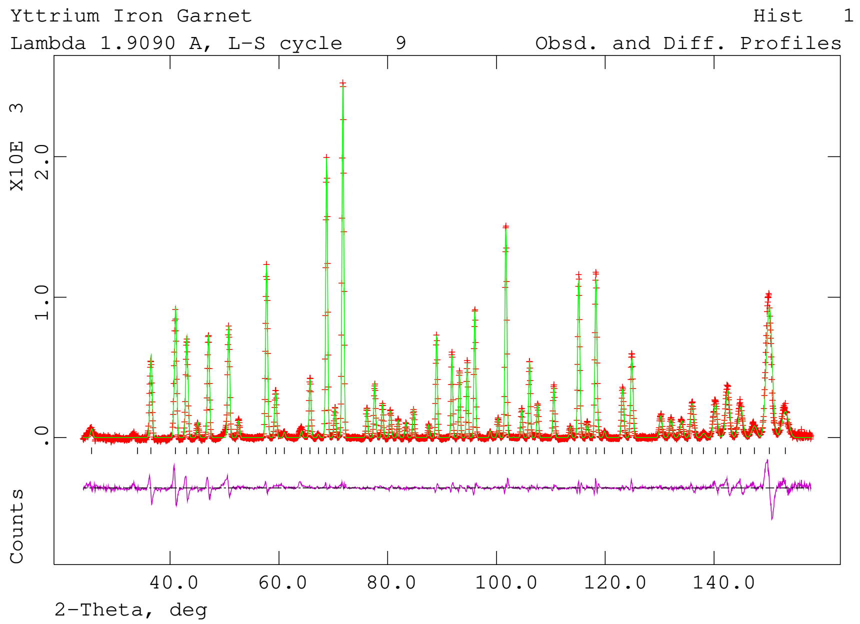
As you can see the fit at this point is quite poor and more parameters need to be varied before the fit will improve. Close examination of the difference curve indicates that a lot of the error arises from lattice parameter and zero point. The list output shows that while the refinement converged rapidly, 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.

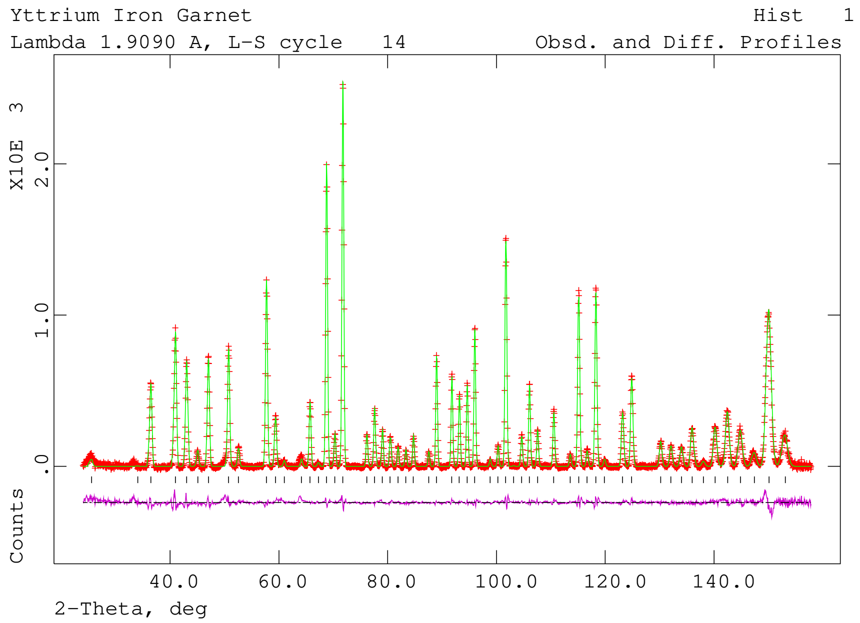


Examination of the fit seems to indicate that the major differences are related to structural details and profile shapes. Notice that several peaks have the wrong calculated intensity; this indicates a structural problem. In this case it is probably a combination of positional errors for the oxygen atom, atom fractions for the iron/aluminum sites and thermal parameters for all atoms. We suggest that you refine all of these first; you should also increase the maximum number of L-S cycles to five. The atom constraints that 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 (<?>,A,B,C,D,E,J,L,P,V,X) >
```

Enter ëEí 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 ë1í 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 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 Rietveld 1 or 2 for LeBail
(1-model weighted, 2-start all Fo=1.0)
Damping factor for LeBail extraction:    0
(to be applied only to 1st cycle)
Fo extraction flag editing options - (<?>,C,D,E,H,L,N,X) >
```

There are two techniques available in GSAS for the extraction of $F_O$ís 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 $F_o$ís so that meaningful difference Fourier maps can be produced to locate missing atoms, etc. The ìle Bailî method begins with either a set of calculated structure factors based on a partial or dummy structure or else a set of identical structure factors to obtain an initial set of $F_o$ís. On subsequent least-squares cycles the set of $F_o$ís extracted from one cycle are used as the $F_c$ís 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 extraction will occur and that "normal" is the default method. Enter ë↵í 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) >
```

As the flags are already set for you by default, you do not need to do anything here so enter ëX X Xí to return back 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 ëFí to select this option.

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

The available Fourier calculations include Patterson (ëPTSNí), difference Patterson (ëDPTSí), observed Fourier (ëFOBSí), difference Fourier (ëDELFí), calculated Fourier (ëFCLCí) and modified difference (ëNFDFí) maps. The Patterson functions 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 ëFOBSí.

```
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 ëXí for sections spaced along the *a*-axis. 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 ë↵í 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 ë/í. This choice ensures that the contouring routine FORPLOT 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  12.188950 A
The new del-x is   .2031 A
The cell will be divided into   60 points along x
The b-axis is  12.188950 A
The new del-y is   .2031 A
The cell will be divided into   60 points along y
The c-axis is  12.188950 A
The new del-z is   .2031 A
The cell will be divided into   60 points along z
Old x limits are   .0000 to   .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 ë-1/8   1/8í.

```
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 ë-1/8   1/8í.

```
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 ë0   1/4í.

```
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 ë1   0í to include it and terminate the list.

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

This is the main Fourier control menu; enter ë↵í 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
 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 option (<?>,A,D,E,F,H,I,L,P,R,S,T,W,X) >
```

Each of the items you have just entered can be now edited from this menu. Enter ëLí 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  .2031 A; the range is  -.1250 to   .1250
Divide the cell into   60 points along y
The y interval is  .2031 A; the range is  -.1250 to   .1250
Divide the cell into   60 points along z
The z interval is  .2031 A; the range is   .0000 to   .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 option (<?>,A,D,E,F,H,I,L,P,R,S,T,W,X) >
```

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

The next section of this manual describes the map display program FORPLOT but first you need to calculate the Fourier. At the GSAS prompt on a Unix system enter ëfourier'; in Windows select ëFourierí from the ëComputeí pull down menu.

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 in Unix type ëforplotí at the main GSAS prompt; for Windows find ëForplotí in the ëGraphicsí pull down menu. The following will be displayed.

```
                |-----------------------------------------------|
                |          Program FORPLOT Version MS-DOS       |
                | Crystal structure Fourier map drawing program |
                | Distributed on 28/ 6/2000; 0:34:42            |
                |-----------------------------------------------|
        |---------------------------------------------------------------|
        |           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, 2000, The Regents of the University of California. |
        |---------------------------------------------------------------|

Enter terminal type (<?>,A,B,Z) >
```

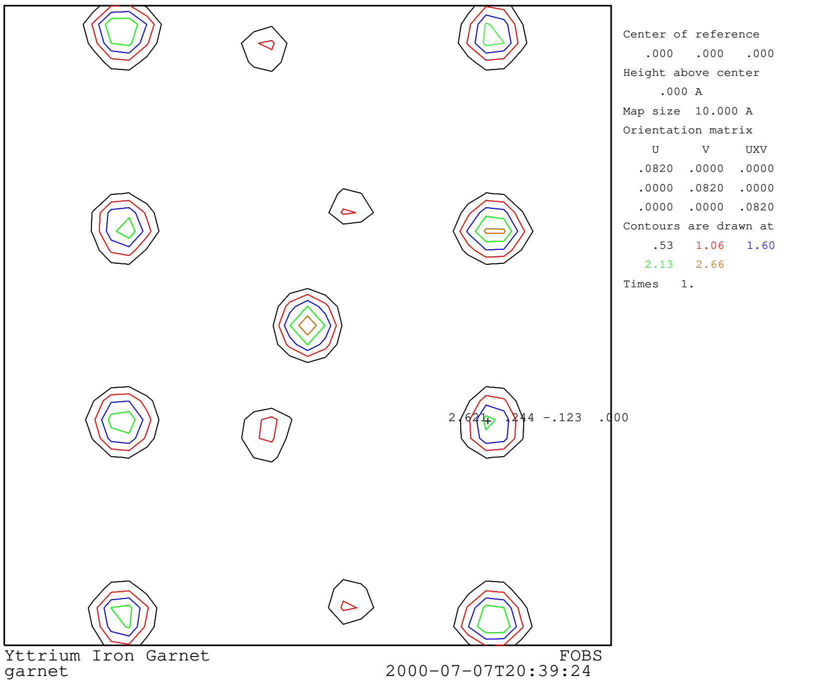
As in the earlier exercises with EXPEDT and POWPLOT, you need to identify the type of graphics terminal you are now using. Enter the appropriate letter. FORPLOT will read the map file output by FOURIER and show you a summary of what it found as well as the default plotting parameters.

```
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 pixels in the map. The rest of the display shows the default settings. FORPLOT has selected 5 contours that 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 ëلí 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
 O      - Convert map to DSN6 format
 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 (ëGí, ëIí, ëNí and ëMí), another the map orientation and position (ëAí, ëCí, ëH', ëRí and ëVí) and the rest provide information. To see the default plot type ëPí and the contoured plot will immediately follow.



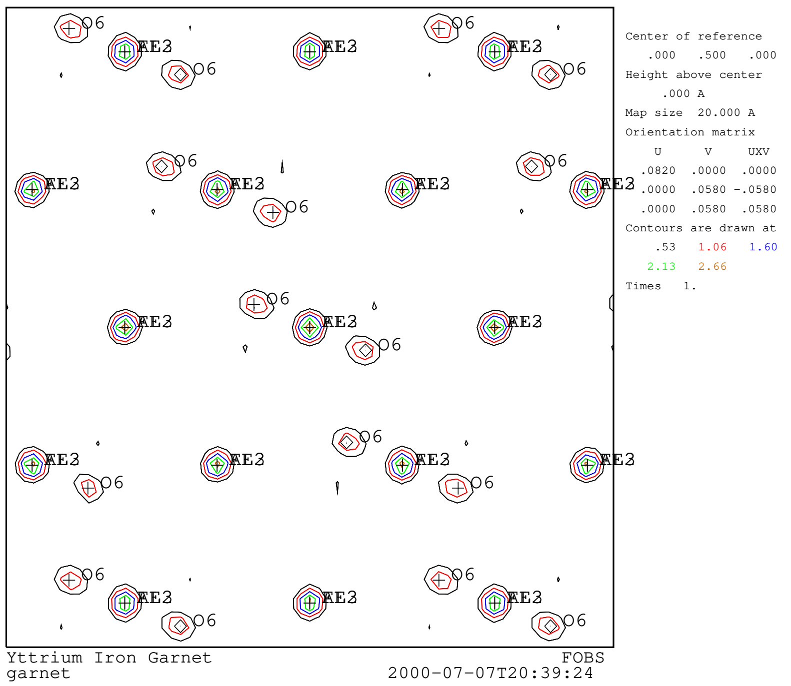
This is a 10 x 10 *ab*-section centered at 0,0,0 looking down the *c*-axis of the garnet cell. The peak in the center is the first Fe/Al atom, the smaller peaks nearby are close to the O atom positions and the intermediate peaks to the right and left are Y atoms. A graphics cursor and a menu also appears 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 ëWí to show its crystallographic coordinates. They are printed to the right. Then type ëHí to show the density; it is printed to the left. The ëCí 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 ëXí.

```
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 ëV 1 0 0 0 1 1í; this will set the U and V vectors. FORPLOT will then display the new orientation matrix.

```
New grid to crystal transformation matrix:
    .08204     .00000     .00000
    .00000     .05801    -.05801
    .00000     .05801     .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 0.5 of the plot plane to be labeled. All these commands can be entered on one line so type ëC 0 1/2 0 S 10 D 0.5 Pí, the plot will immediately follow.



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 ëRí commands are cumulative, that is each rotation is applied to the previous orientation to give a new one. A ëVí or ëAí command starts a new orientation and wipes out the effect of any previous ëRí commands. The height option ëHí 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 ëIí and ëNí options. Changing the minimum density with the ëMí option will not generate extra contour levels until an ëIí option is given, and ëMí has no effect on the contour levels set with the ëNí option..

Distance-Angle Setup and Calculations

There is a set of controls for a distance/angle calculation that 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 ëDí 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 ë?í 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 ëDí 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         .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 ëCí option. You also have the choice of using overall limits for both distance and angle calculations. This choice is also made with the ëCí option. Enter ë?í 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 ëXí a sufficient number of times to exit EXPEDT.

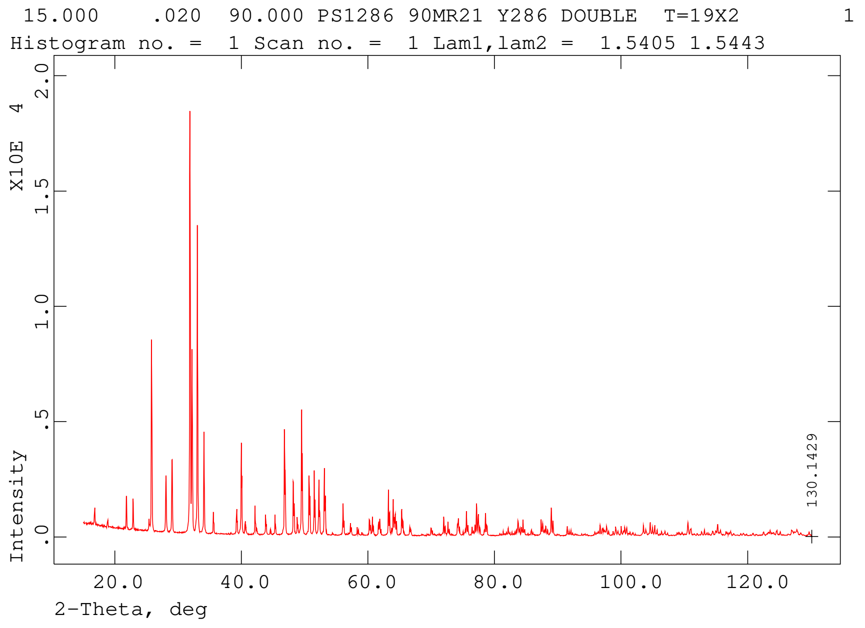
To run the distance/angle program in Unix enter ëdisaglí at the GSAS; for Windows select the ëDisaglí option in the ëResultsí pull down menu. The output will be appended to the list file and can be examined after the job completes.

X-Ray Powder Diffraction – Fluoroapatite

In this training exercise you will refine the structure of fluoroapatite using constant wavelength X-ray powder diffraction data. At the completion of the refinement you will then prepare a Virtual Reality drawing of the fluoroapatite structure. The structure is hexagonal with four different kinds of atoms spread over seven different sites. The data was taken on a conventional Bragg-Brentano powder diffractometer using CuK_α radiation. It is presumed that you have already done the nickel and garnet powder examples 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 X-ray powder data is essentially identical to that for CW and TOF neutron data as given in the nickel and garnet exercises. After entering the GSAS command and naming the experiment (ëfapí would be a suitable name) type or select ëexpedtí to start data preparation. As before the powder data preparation option ëPí is used to introduce new data to the system. The space group for this garnet is ëP 63/mí (i.e. $P6_3/m$) and the hexagonal lattice parameters are a=í9.37í and c=í6.88í. The unit cell contains 10 Ca atoms, 6 P atoms, 2 F atoms and 24 O atoms scattered over 7 sites. The raw data can be found in the file ë/gsas/example/FAP.XRAí and the instrument file is ë/gsas/example/INST_XRY.PRMí. There is only one histogram corresponding to a scan from 15˚ to 130˚ 2Θ in steps of 0.20˚ 2Θ giving 5751 points. The scan number for this histogram is ë1í and the corresponding instrument parameter set is also ë1í. A plot of the entire histogram is shown below; a point at the maximum 2Θ was marked with the cursor option ëWí.



Powder Data Preparation and Refinement

For constant wavelength data 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 ëTí option and give a maximum 2Θ of ë131í that is just beyond the end of the data.

```
Change profile parameter values and refinement flags
Histogram no.   1 Bank no.  1 Lambda1,lambda2 =  1.54050 1.54430
Title:  15.000    .020  90.000 PS1286 90MR21 Y286 DOUBLE  T=19X2
Histogram is not ready to be used in least-squares
Minimum d-spacing must be set before processing by POWPREF

Phase no. 1
Phase name: fap
Aniso. broadening axis   0.   0.   1. Damp  0
Peak profile type no. 2 Number of coefficients: 18
Profile coefficients for Simpson's rule integration of pseudovoigt function
C.J. Howard (1982). J. Appl. Cryst.,15,615-620.
P. Thompson, D.E. Cox & J.B. Hastings (1987). J. Appl. Cryst.,20,79-83.
#1(GU)    =      2.0 N #2(GV)    =     -2.0 N #3(GW)    =      5.0 N
#4(LX)    =    1.000 N #5(LY)    =    1.000 N #6(trns)  =     .000 N
#7(asym)  =    .0000 N #8(shft)  =    .0000 N #9(GP)    =       .0 N
#10(stec)=       .00 N #11(ptec)=       .00 N #12(sfec)=       .00 N
#13(L11)  =     .000 N #14(L22)  =     .000 N #15(L33)  =     .000 N
#16(L12)  =     .000 N #17(L13)  =     .000 N #18(L23)  =     .000 N
Cut-off for peaks is  1.00 percent of the peak maximum
Profile editing options - (<?>,$,A,C,L,P,R,W,X) >
```

The profile function set up for this Rietveld refinement is the one with the pseudo-Voigt description of the profile shape. The values given for ëGUí, ëGVí and ëGWí are typical for modern commercial Bragg-Brentano diffractometers and the values for ëLXí and ëLYí are reasonable starting values for the sample broadening.

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) >
```

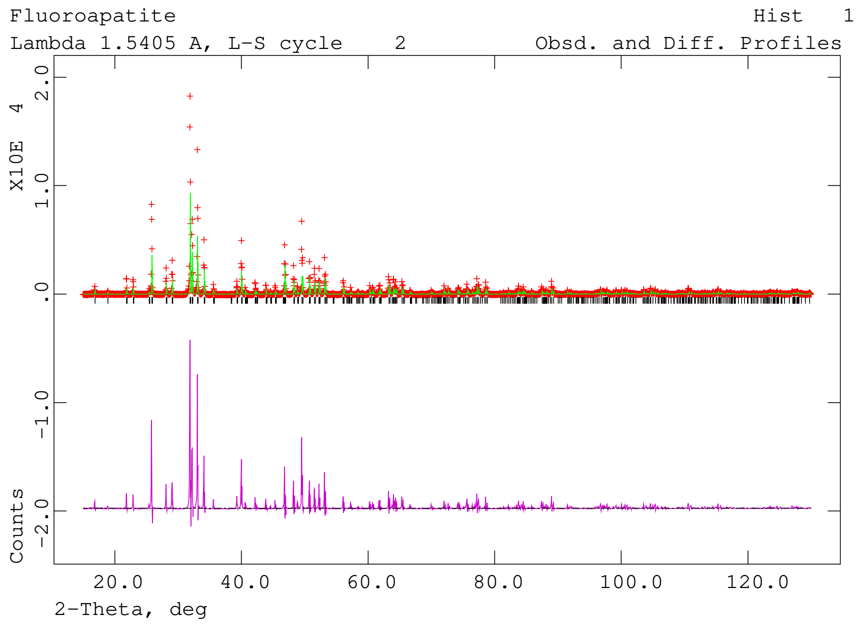
At this point you can continue your editing session by entering ëLí to start editing of least squares data. As before you will need to enter some atoms, check the least squares controls and perhaps examine the defaults for the other parameters. The atoms you will need to enter are:

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM MULT FXU
  1 CA    .33333  .66667  .00100 1.00000 CA1       .00500 I        3     4 000
  2 CA    .24200  .99200  .25000 1.00000 CA2       .00500 I     M(001)   6 000
  3 P     .39700  .36700  .25000 1.00000 P3        .00500 I     M(001)   6 000
  4 F     .00000  .00000  .25000 1.00000 F4        .01000 I       -6     2 000
  5 O     .32500  .48500  .25000 1.00000 O5        .00500 I     M(001)   6 000
  6 O     .59100  .46900  .25000 1.00000 O6        .00500 I     M(001)   6 000
  7 O     .34000  .25800  .07000 1.00000 O7        .00500 I        1    12 000
```

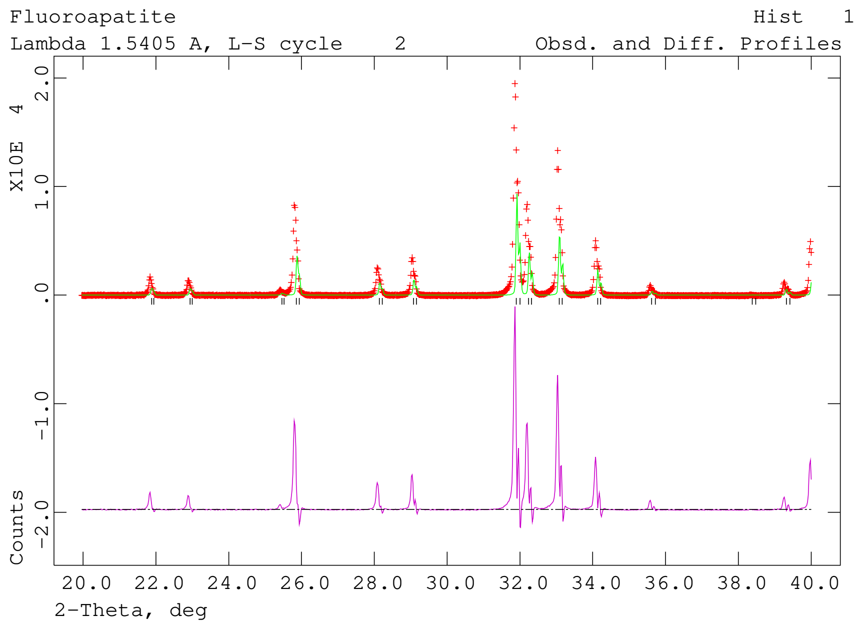
This listing is obtained by entering ëLí after you have entered all the atoms for this example. The values of U_{iso} are a reasonable guess for this. The atom positions for the first Ca atom were entered as fractions (i.e. ë1/3 2/3 0í). After finishing with atom input, it will be useful to change the number of cycles to 5. Next the background function should be changed to function #5 with three coefficients; this will give a better fit to the background that seems to rise both at low and high 2Θ. Exit from EXPEDT and run POWPREF and GENLES. The last cycle output from GENLES is shown below and the profile fit is shown in the next figure.

```
Restraint data statistics:

Powder data statistics                Fitted         -Bknd             Average
             Bank Ndata Sum(w*d**2)  wRp     Rp    wRp     Rp     DWd  Integral
Hstgm  1 PXC    1  5750 6.20717E+05  .5828  .4835  .7216  .6278    .240    .964
Powder totals      5750 6.20717E+05  .5828  .4835  .7216  .6278    .240
Cycle   2 There were  5750 observations. Total before-cycle CHI**2 = 6.2072E+05

Reduced CHI**2 =  108.0      for     4 variables
Histogram  1  Type PXC   Nobs=  652 R(F**2) =   .6389

Final variable sum((shift/esd)**2) for cycle   2:        .00 Time:    1.21 sec

Convergence was achieved and
GENLES terminated successfully
```

The first plot from POWPLOT is of the full scan; it is evident that the fit is quite poor.



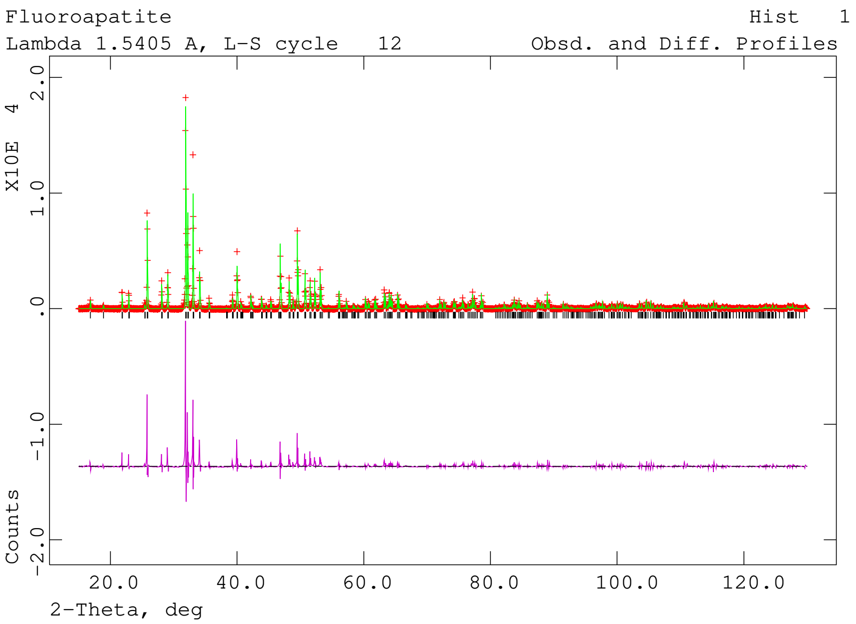
The next plot shows the region from 20˚ 2Θ to 40˚ 2Θ.



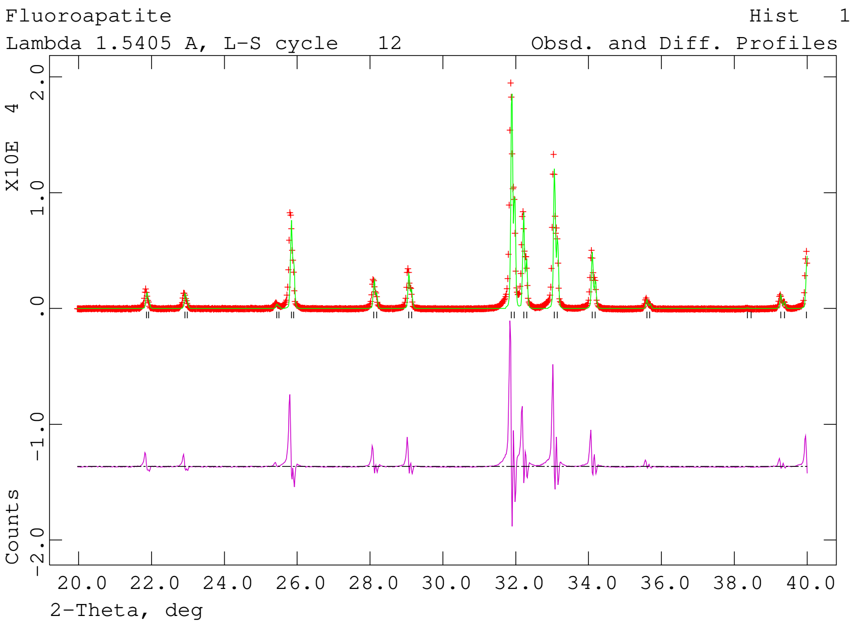
Inspection of the misfit between the observed and calculated profiles shows that it is mostly due to a slight offset in the peak positions and that the calculated profiles are not as wide as the observed ones. You should refine the lattice parameters first to get the positions of the reflections corrected. Run GENLES then POWPREF and then GENLES again. The first GENLES run will not come to convergence, but there will have been a sufficient improvement in the fit to warrant proceeding to POWPREF and then GENLES. This time GENLES nearly converges; the final cycle is shown below.

```
Restraint data statistics:

Powder data statistics                Fitted         -Bknd              Average
             Bank Ndata Sum(w*d**2)  wRp      Rp     wRp      Rp      DWd  Integral
Hstgm  1 PXC   1  5750 2.69248E+05  .3839  .2950  .4433  .3521    .347     .956
Powder totals     5750 2.69248E+05  .3839  .2950  .4433  .3521    .347
Cycle  12 There were  5750 observations. Total before-cycle CHI**2 = 2.6925E+05

Reduced CHI**2 =  46.87     for     6 variables
Histogram  1  Type PXC   Nobs=  652 R(F**2) =   .2975

Final variable sum((shift/esd)**2) for cycle  12:        .54 Time:    1.21 sec

GENLES terminated successfully
```

The full profile from POWPLOT is shown next.



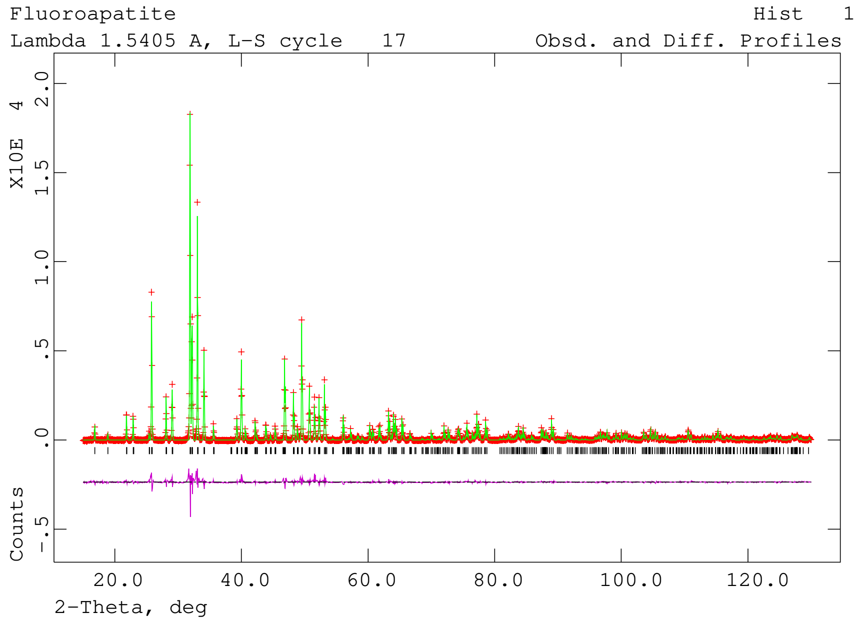
The next plot shows the region from 20˚ 2Θ to 40˚ 2Θ.



The fit is still quite poor but it is much better that before. The major problem now seems to be that the calculated profiles are not wide enough and that there is still some peak displacement error. The appropriate profile coefficients to vary are the Lorentzian coefficients ëLXí (particle size), ëLYí (microstrain) and ëshftí (sample displacement). Then run POWPREF and GENLES. The last cycle of least squares shows marked improvement.

```
Restraint data statistics:

Powder data statistics                Fitted         -Bknd              Average
             Bank Ndata Sum(w*d**2)  wRp      Rp     wRp      Rp      DWd  Integral
Hstgm  1 PXC   1  5750  36032.      .1404  .0938  .1222  .0879    .522    .892
Powder totals     5750  36032.      .1404  .0938  .1222  .0879    .522
Cycle  17 There were  5750 observations. Total before-cycle CHI**2 = 3.6032E+04

Reduced CHI**2 =  6.276     for     9 variables
Histogram  1  Type PXC   Nobs=  652 R(F**2) =   .0840

Final variable sum((shift/esd)**2) for cycle  17:        .00 Time:    1.21 sec

Convergence was achieved and
GENLES terminated successfully
```

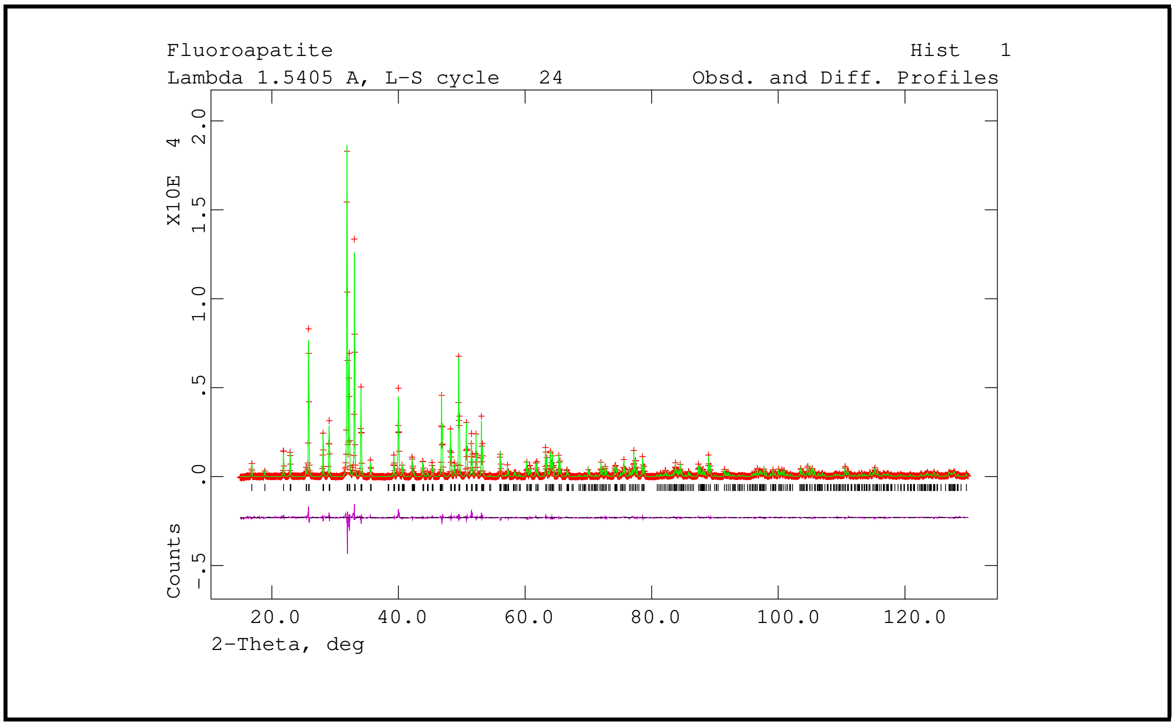
Next is the full profile from POWPLOT.



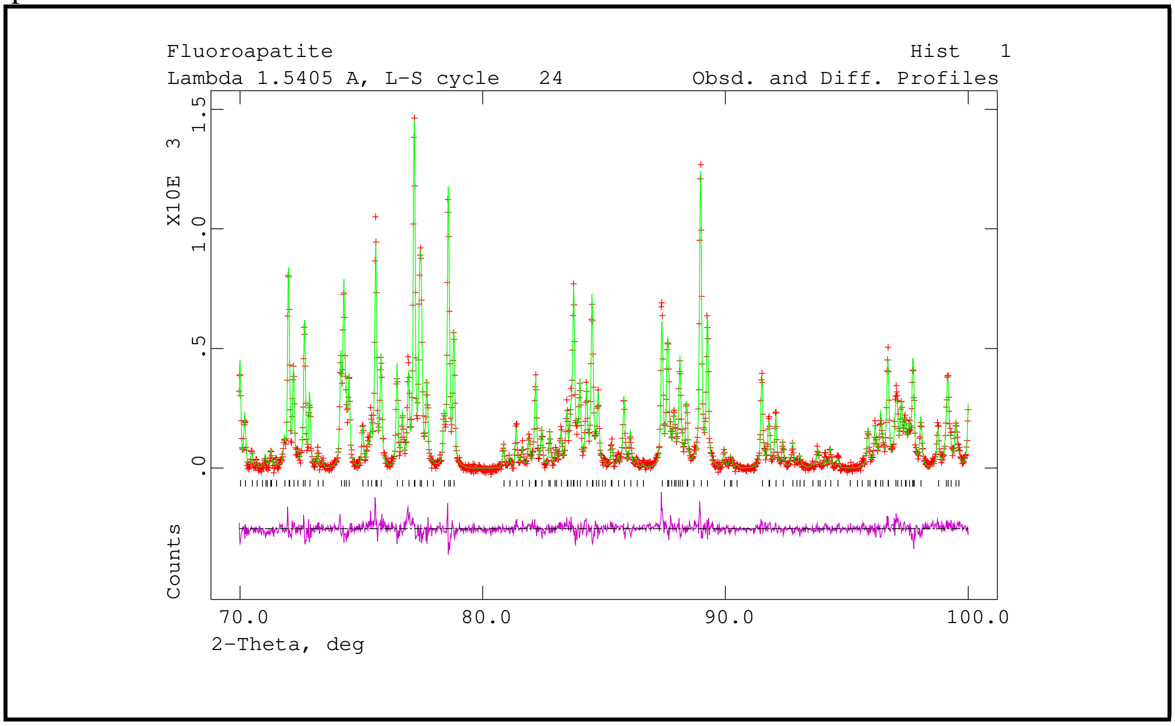
Clearly the fit is much improved. Careful examination of the profiles (you should look at 5-10° segments of the pattern for this) shows a slight asymmetry for the profiles for the lowest angle peaks; profile parameter ëasymí should be refined for this. In addition the calculated profiles for each peak are cut off well before the observed profiles fall to the base line. To fix this the profile cutoff should be changed to 0.5% (default is 1%). The anisotropic contributions for the Lorentzian broadening (ëstecí and ëptecí) should also be refined at this time. In addition, one can refine the atom coordinates and thermal parameters. Run POWPREF and GENLES each twice to achieve convergence.

```
Restraint data statistics:

Powder data statistics              Fitted          -Bknd              Average
             Bank Ndata Sum(w*d**2)  wRp      Rp     wRp      Rp      DWd  Integral
Hstgm  1 PXC    1  5750  16581.      .0953  .0724  .0862  .0699    .929    .949
Powder totals      5750  16581.      .0953  .0724  .0862  .0699    .929
Cycle  24 There were  5750 observations. Total before-cycle CHI**2 = 1.6581E+04

Reduced CHI**2 =  2.899     for    31 variables
Histogram  1  Type PXC   Nobs=  657 R(F**2) =   .0655

Final variable sum((shift/esd)**2) for cycle  24:        .00 Time:    1.59 sec

Convergence was achieved and
GENLES terminated successfully
```

As you can see from the final GENLES cycle the fit is quite good as is also evident in the profile plot from POWPLOT.



An expanded view of a selected high angle portion of the pattern shows how well the profile has been fitted.



You may wish to try to improve the refinement further, however for the purposes of this exercise we will continue on with use of the program VRSTPLOT for creating a Virtual Reality file of the crystal structure.

Drawing the Structure of Fluoroapatite with VRSTPLOT

The object here is to produce a Virtual Reality drawing of the structure of fluoroapatite. We want to draw the unit cell contents showing space filling balls for the Ca and F atoms and show the PO_4^{3-} anions as tetrahedra. To start the program, enter for Unix ëvrstplotí at the GSAS prompt or select ëVrstplotí in the ëGraphicsí pull down menu for Windows. The opening screen will then appear.

```
                    |----------------------------------------|
                    |     Program VRSTPLOT Version MS-DOS     |
                    | VRML crystal structure plotting program |
                    | Distributed on 10/ 7/2000; 5:21:48      |
                    |----------------------------------------|

        |----------------------------------------------------------------|
        |            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, 2000, The Regents of the University of California. |
        |----------------------------------------------------------------|

Enter <CR> to continue >
```

Enter ë↵í to continue. The crystal structure data for fluoroapatite will be read in.

```
Phase name: FAP
Lattice parameters:
a,b,c            =     9.3726    9.3726    6.8865
alpha,beta,gamma =     90.000    90.000   120.000

Space group   P 63/m
The lattice is centric   primitive hexagonal     Laue symmetry 6/m
 Multiplicity of a general site is  12
 The symmetry of the point 0,0,0 contains 1bar

The equivalent positions are:

( 1)      X       Y       Z   ( 2)     X-Y      X  1/2+Z  ( 3)     -Y      X-Y      Z
( 4)     -X      -Y  1/2+Z   ( 5)     Y-X     -X      Z   ( 6)      Y      Y-X 1/2+Z

Enter <CR> to continue >
```

First the lattice parameters and the space group information for fluoroapatite are displayed; enter ë↵í to continue.

```
Atomic coordinates (Uij*100):
ser.   x       y       z     name      U11    U22    U33    U12    U13    U23
  1   .3333   .6667   .0017 CA1         .57    .00    .00    .00    .00    .00
  2   .2419   .9925   .2500 CA2         .42    .00    .00    .00    .00    .00
  3   .3974   .3677   .2500 P3          .36    .00    .00    .00    .00    .00
  4   .0000   .0000   .2500 F4         1.35    .00    .00    .00    .00    .00
  5   .3248   .4845   .2500 O5          .48    .00    .00    .00    .00    .00
  6   .5914   .4697   .2500 O6          .61    .00    .00    .00    .00    .00
  7   .3396   .2580   .0707 O7          .61    .00    .00    .00    .00    .00
Space filling atoms will not be plotted
Thermal ellipsoids will be plotted
The ellipsoid probability is     .500
Unit cell edges will not be plotted
Enter VRSTPLOT command (<?>,A,B,C,E,F,H,L,M,N,P,U,W,Q) >
```

Next the atom coordinates are listed along with default settings for some of the drawing parameters. Enter ë↵í to see the help listing.

```
VRSTPLOT commands:
 <?>   - Type this help listing
 A     - Select atoms for drawing
 B     - Select bonds for drawing
 C     - Modify atom colors
 E     - Toggle plot of space filling atoms or ellipsoids
 F     - Setup plot of Fourier contours
 H     - Toggle of hkl plane plot
 L     - List structure data
 M     - Change ellipsoid probability or atom radius multiplier
 N n   - Select a new phase n
 P     - Select polyhedra for drawing
 U     - Toggle plot of unit cell edges
 W     - Write VRML plot file
 Q     - Quit VRSTPLOT
Enter VRSTPLOT command (<?>,A,B,C,E,F,H,L,M,N,P,U,W,Q) >
```

There are different kinds of commands in this menu. ëAí, ëBí and ëPí are for selection of structural objects to draw. ëFí is used to setup the drawing of Fourier map contours superimposed on the structure. ëHí can be used to show the relationship between a set of hkl reflection planes and some structural feature. Most of the other commands are toggles to change the way atoms are displayed or even select different colors for the atoms. To begin the setup for the drawing you need to select the set of atoms to draw. Enter ëAí to begin.

```
List of atoms to be plotted
No atoms in drawing array
Atom names:
   1 CA1         2 CA2         3 P3          4 F4          5 O5
   6 O6          7 O7
Enter atom selection control (<?>,A,L,U,X) >
```

You are told there are no atoms to be drawn, you will add some shortly. Enter ë↵í to see the choices.

```
Atom selection commands
 <?>   - Type this help listing
  A    - Individual atoms
  L    - Show list of selected atoms
  U    - All atoms within unit cell
  X    - Exit atom selection
Enter atom selection control (<?>,A,L,U,X) >
```

Atoms can be added individually or by selecting those within a block of unit cells. We want to draw one unit cell of fluoroapatite so enter ëUí.

```
Enter atom seq. or type to be included >
```

We want the drawing to include the Ca, P and F atoms; enter ë1:4í to include them.

```
Enter minimum and maximum along X axis >
```

VRSTPLOT will next ask for the range in Y and Z; to get one unit cell enter ë0 1 0 1 0 1í.

```
List of atoms to be plotted
 At.No.  Designator    At.No.  Designator    At.No.  Designator
     1    1(   1 0 0 0)      2    1(   2 1 0 0)      3    1(  -1 1 1 1)
     4    1(  -2 0 1 1)      5    2(   1 0 0 0)      6    2(   2 1 0 0)
     7    2(   3 1 1 0)      8    2(   4 1 1 0)      9    2(   5 0 1 0)
    10    2(   6 0 0 0)     11    3(   1 0 0 0)     12    3(   2 0 0 0)
    13    3(   3 1 0 0)     14    3(   4 1 1 0)     15    3(   5 1 1 0)
    16    3(   6 0 1 0)     17    4(   1 0 0 0)     18    4(   1 0 1 0)
    19    4(   1 1 0 0)     20    4(   1 1 1 0)     21    4(   2 0 0 0)
    22    4(   2 0 1 0)     23    4(   2 1 0 0)     24    4(   2 1 1 0)
Atom names:
   1 CA1         2 CA2         3 P3          4 F4          5 O5
   6 O6          7 O7
Enter atom selection control (<?>,A,B,D,L,R,U,X) >
```

VRSTPLOT found 24 atoms within the unit cell. Notice that we did not include the O atoms. The plan is to draw the PO_4^{3-} groups as tetrahedra so they are not included here. Enter ëXí to return to the main menu.

```
Enter VRSTPLOT command (<?>,A,B,C,E,F,H,L,M,N,P,U,W,Q) >
```

The ëPí option is for selection of polyhedra for drawing, enter that now.

```
List of polyhedra to be plotted
No polyhedra in drawing array
Atom names:
  1 CA1        2 CA2        3 P3         4 F4         5 O5         6 O6
  7 O7
Enter polyhedron selection control (<?>,B,D,L,X) >
```

There arenít any polyhedra defined; you will add some now. Enter ë↵í to see the menu.

```
Polyhedron selection commands
 <?>   - Type this help listing
  B    - All polyhedra with "bond" distance
  L    - Show list of selected polyhedra
  X    - Exit polyhedron selection
Enter polyhedron selection control (<?>,B,D,L,X) >
```

To select polyhedra to be drawn enter ëBí.

```
Enter origin atom seq. or type >
```

Polyhedra are defined by specifying the central atom first; these must be inserted in the atom drawing list. We earlier added the P atoms to the atom drawing list, now enter ëPí to specify the central atom of the PO_4^{3-} tetrahedra.

```
Enter target atom seq. or type >
```

The vertices of the polyhedra are specified next. For PO_4^{3-} these are the O atoms; enter ëOí now.

```
Enter bond length for polyhedron >
```

Next is the length of the internal polyhedron bond for the vertices search. For a PO_4^{3-} tetrahedron this is the length of the P-O bond; enter ë1.5í.

```
Enter tolerance in bond length >
```

As one may not know exactly what value to choose for this internal polyhedral bond length, VRSTPLOT asks for a range in this bond length. Enter í0.2í so that bonds of 1.3-1.7A are selected.

```
    4 polyhedra added to drawing list
List of polyhedra to be plotted
No. Ori. Tar. Dist.         Vector      No. Ori. Tar. Dist.         Vector
  1    3    5 1.5505 -.0726  .1168  .0000   2    3    6 1.5751  .1940  .1019  .0000
  3    3    7 1.5226 -.0578 -.1097 -.1793   4    3    7 1.5226 -.0578 -.1097  .1793
Atom names:
  1 CA1        2 CA2        3 P3         4 F4         5 O5         6 O6
  7 O7
Enter polyhedron selection control (<?>,B,D,L,X) >
```

VRSTPLOT then lists the polyhedral bond found in its search. Since we are drawing PO_4 tetrahedra we are expecting to have just four bonds. The listing shows that many so the search was successful. Enter ëXí to return to the main menu.

```
Unit cell edges will be plotted
Enter VRSTPLOT command (<?>,A,B,C,E,F,H,L,M,N,P,U,W,Q) >
```

Next we want to have the unit cell edges drawn and use space filling atoms at 0.3 of their full radius. Enter ëU E M 0.3í; the output will show the state of each toggle as they are changed.

```
Unit cell edges will be plotted
Thermal ellipsoids will not be plotted
Space filling atoms will be plotted
Atom radius factor is    1.000
The new atom radius factor is    .30
Enter VRSTPLOT command (<?>,A,B,C,E,F,H,L,M,N,P,U,W,Q) >
```

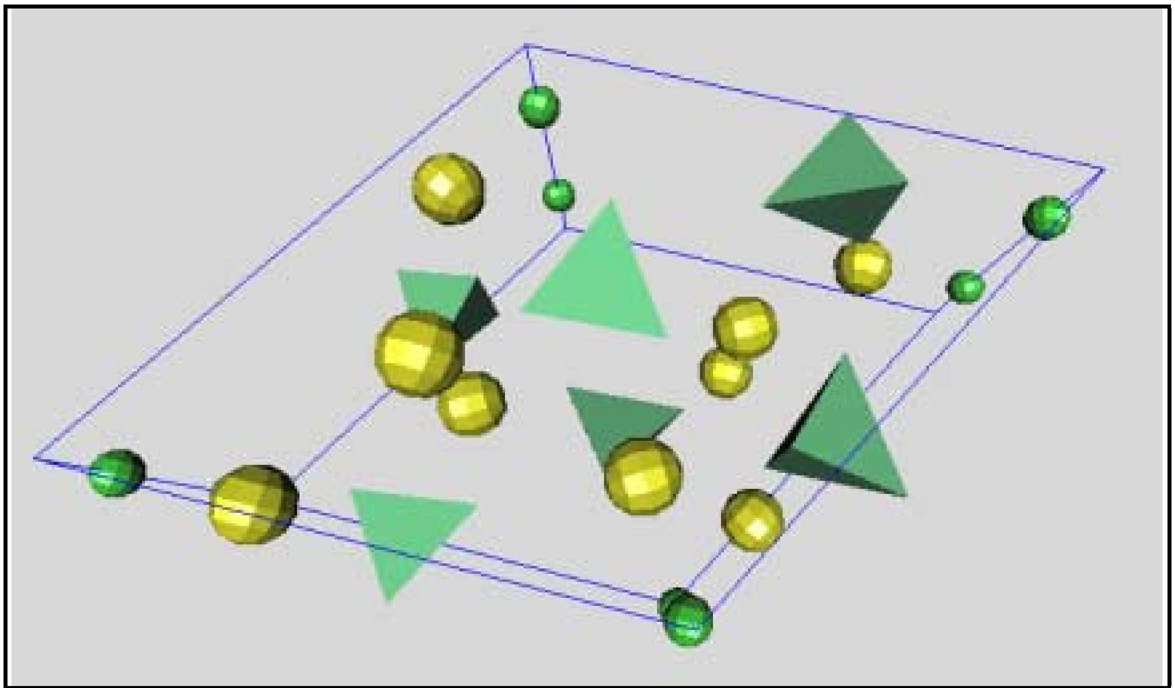
To write the Virtual Reality file enter ëWí; you will then be asked to select a background color.

```
The color number for the background is  54 (Gray85           )
Enter new color number (1–120, 0 for list) >
```

Enter ë/í to select the default background (a very light gray).

```
The VRML .wrl file has been written, you may
now view it with your favorite viewer.
Enter VRSTPLOT command (<?>,A,B,C,E,F,H,L,M,N,P,U,W,Q) >
```

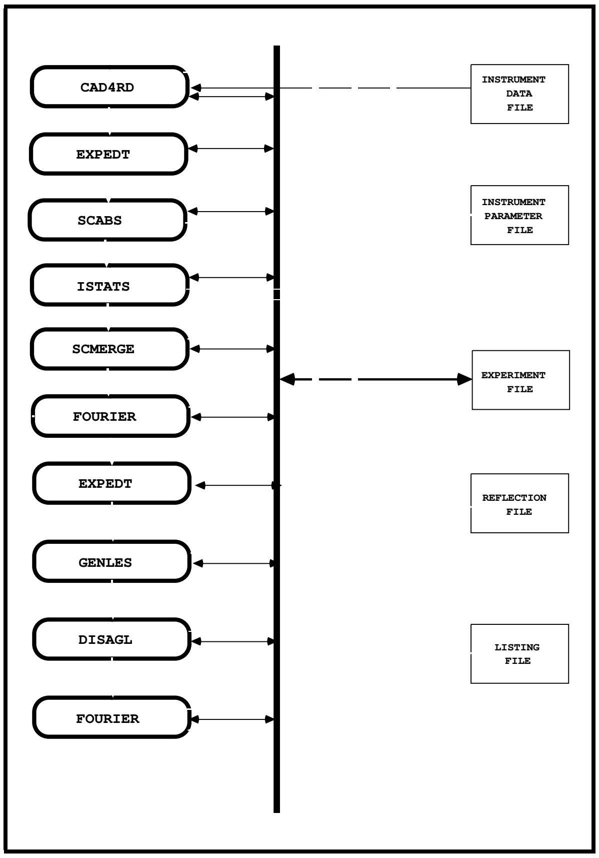
The file FAP.WRL has been written into your working directory. It can now be read by your favorite VRML viewer. The plot shown next was produced by VRWeb which works well with these files in Windows.



The Ca atoms are drawn in yellow, the F atoms in green and the PO_4^{3-} tetrahedra are also green; this color is associated with the P atom. The unit cell edges are also drawn. Notice that VRSTPLOT is still open, so that you can change the drawing interactively. A new ëWí command overwrites the old FAP.WRL file and you will need to reread it to see any changes you make. Enter ëQí to finish working with VRSTPLOT.

Single Crystal X-Ray Data – Oxonium Hexafluoroantimonate

As an introduction to the use of GSAS to process single crystal data, we present first a flow diagram for the sequence of GSAS routines that 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 that 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 an Enraf-Nonius CAD4 single crystal diffractometer.

Processing Single Crystal Data

Unlike the powder diffraction examples shown above, processing single crystal diffraction data normally starts with a routine designed to read one of several single crystal raw data formats. These routines are CAD4RD, P3R3DATA and SXTLDATA. The first two are for reading data obtained on specific manufacturerís instruments while the third is a more general-purpose routine that can read reflection data from any fixed format ASCII file. For Unix, enter the GSAS command and name the experiment (ëOXONí is assumed here). Then enter ëcad4rdí to begin the data preparation. For Windows ëCad4rdí can be found in the ëSetupí pull down menu. You will get the first prompt.

```
Experiment - OXON - was not found in directory
C:\GSAS\TESTS
Do you wish to create it (Y/<N>)? >
```

You want to create the file OXON.EXP, so enter ëYí 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 - OXON - has been created.
 Enter a title for this experiment
  >
```

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

```
            |-------------------------------------------------------|
            |            Program CAD4RD Version MS-DOS              |
            |        Convert CAD4 data to a standard form           |
            | Modified by James Fait, University of Calgary Apr 89  |
            |             Modified by ACL Feb, Apr 90               |
            |       Distributed on 28/ 6/2000; 0:33:50              |
            |-------------------------------------------------------|

        |----------------------------------------------------------------|
        |           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, 2000, The Regents of the University of California. |
        |----------------------------------------------------------------|

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

The file ë/gsas/example/CAD4.PRMí is the instrument parameter file for the CAD4. It contains information that characterizes the Enraf-Nonius CAD4 diffractometer including attenuator data and the sense of rotation of the goniometer circles. Notice that the possibility of executing system commands is available here (the ë$í command).

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

The next prompt is for the CAD4 data file that contains both the results of the lattice parameter and orientation matrix determination as well as the entire data acquisition results. Enter ë/gsas/example/OXONIUM.DATí 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 ë↵í to accept it.

```
There is no phase information present
*** No phase exists ***
Enter phase edit command(<?>,$,I,R) >
```

We need to enter some phase information as a first step in this process, so enter ëIí to begin.

```
Enter identifying name for new phase number 1.
  >
```

The first request is for a name of this phase, ë(H3O)+(SbF6)-í 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 ëi b 3í 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 ë10.12í and a full list of the lattice constants and calculated cell volume is shown next.

```
Lattice parameters are
    a,b,c  = 10.120000 10.120000 10.120000
    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,R,S,X) >
```

Enter ë?í or ë↵í 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 - Modify phase type flag for phase "n"
 L   - List phase names
 R   - Read phase info. from another experiment file
 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,R,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 ëSí 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 ë.007í and the menu prompt for phase editing is shown.

```
Enter phase edit command(<?>,$,D,E,F,M,I,L,R,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 ëFí.

```
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 ë↵í.

```
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 36 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 ëCí.

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

And now enter ‘h 24 o 8 sb 8 f 48í 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 ë↵í. 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.      .48 +    .48 Lambda
Enter unit cell composition edit command (<?>,$,C,E,F,L,X) >
```

You are finished here so exit formula editing by entering ëXí.

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

You are finished here so exit phase editing by entering ëXí. 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 ë/í 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 =  .70930
 4.1278000E-02 -8.5389000E-02  2.7078000E-02
 9.7240000E-03 -2.5436000E-02 -9.4683000E-02
 8.9162000E-02  4.2269000E-02 -2.5480000E-03
 Lattice constants are 10.1283 10.1404 10.1511   89.93   89.82   89.98
Phi =  344.10 Chi =    91.45 Omega =    64.61
*** WARNING *** ABC(1) was changed to  10.13997
*** WARNING *** ANG(1) was changed to  90.00000
*** WARNING *** ANG(2) was changed to  90.00000
*** WARNING *** ABC(3) was changed to  10.13997
*** WARNING *** ANG(3) was changed to  90.00000

 Nref = 1460 Last iseq = 1926   Exposure time =   79282.  Lambda =  .70930
 4.2096000E-02 -8.4546000E-02  2.8436000E-02
 9.4630000E-03 -2.7169000E-02 -9.4355000E-02
 8.8887000E-02  4.3008000E-02 -3.5850000E-03
 Lattice constants are 10.1209 10.1347 10.1408   90.03   89.91   90.04
Phi =  343.20 Chi =    92.10 Omega =    64.14
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 ëNí.

```
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 enter either ë↵í or ëNí. 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) =                .0029
<abs(del(I))>/Avg(I) =           .0280
rms(del(I))/Avg(I) =             .0316
Sqrt(<I**2>-<I>**2)/<I> is       .0316
Fitting of standards to a polynomial
Default number of terms (M) is:  2 The convergence criterion (C) is:  .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 ë2í.

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

We will use the default convergence criterion of 0.01 by entering ë/í.

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

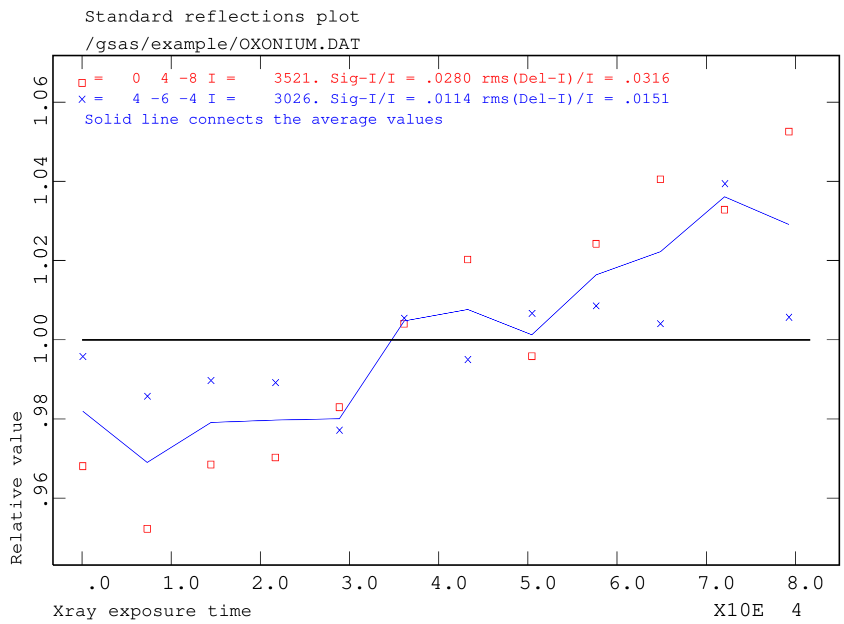
We want the program to search for the best number of terms so enter ëYí.

```
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        -.179548         1.16361        -1.68751         .800540
Errors for polynomial coefficients
    .109520E-01     .171568         .766869         1.21147         .618369
Polynomial evaluated at 0. and  81647.   1.00000   1.09709
rms(del(I))/<I> =                 .0476

Standard no.  2 is     4   -6   -4
It was measured   12 times
Avg(i) = <WI>/<W> is            3026.11
Sigma(I)/Avg(I) =                 .0031
<abs(del(I))>/Avg(I) =            .0114
rms(del(I))/Avg(I) =              .0151
Sqrt(<I**2>-<I>**2)/<I> is        .0151
Number of terms  =  5 Convergence crit. =     .01000
Sum of the squares of the residuals =    9437.25     M =  5

Coefficients of normalization polynomial
    1.00000        -.322341E-01    -.728596E-01     .468899        -.349463
Errors for polynomial coefficients
    .117039E-01     .183042         .817114         1.28995         .658117
Polynomial evaluated at 0. and  81647.   1.00000   1.01434
rms(del(I))/<I> =                 .0136
Plot the standards? (<N>/Y/X=EXIT) >
```

If you are working in Windows some of the above output will have disappeared out the top of the MS-DOS window. 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 ëYí for the first plot.

```
Enter graphic screen option (<?>,A,B,Z) >
```

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



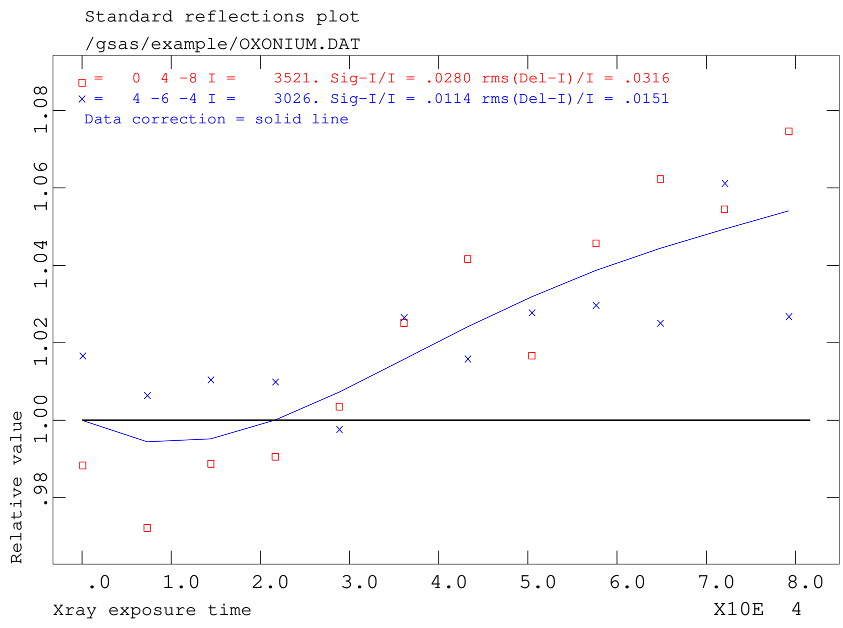
This plot shows the normalized intensities for both standards plotted as symbols along with their average as a solid line. Notice that in this case all three curves are similar so that an average correction is appropriate. On some terminals you need to enter ë↵í to get the next prompt.

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

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

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

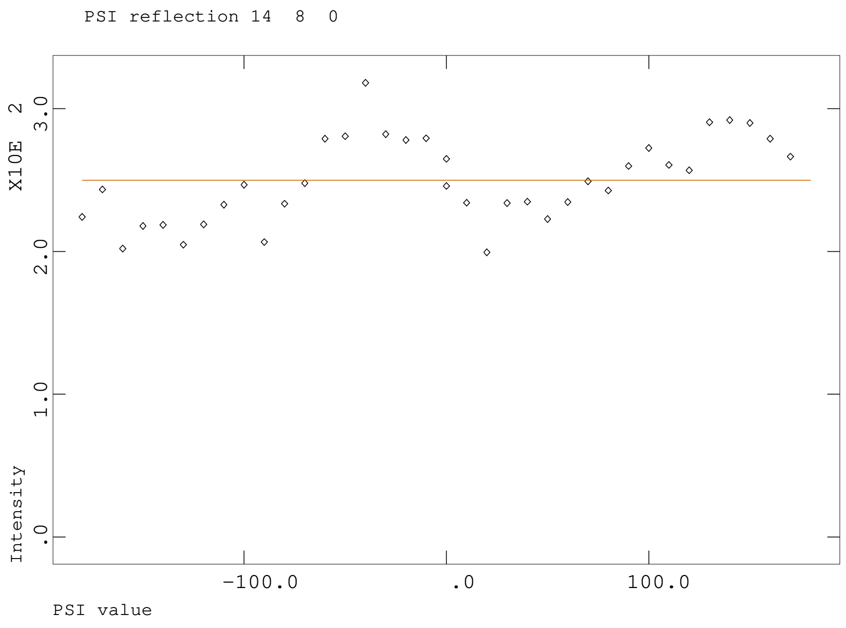
You now need to choose between using the results of the polynomial fit and a simple interpolation of the normalized average standard intensities. Generally the polynomial fit gives a better description of the intensity variations so enter ëYí. A plot of the standards and the polynomial fit will follow.



As you can see the five-term polynomial fit gives a satisfactory description of the intensity variation. As above you may need to enter ë↵í 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 ëYí 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 ë↵í 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 ë/í or ë1í to select it.

```
These measurements, given as IREF, PSI, and Intensity, are
1461    .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    .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 ëYí.

```
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 ëYí.

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

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

```
<sigma(I)>/<I> =    .017
CAD4RD run ended successfully
```

While you were running CAD4RD, it was also reproducing on the list file much of the output seen on the screen. You can examine it by using either of the Unix GSAS utilities ELST or TLST or any Windows text editor.

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 ëexpedtí at the Unix GSAS prompt or else select ëExpedtí from the ëSetupí Windows pull down menu to get started.

```
                  |------------------------------------------|
                  |        Program EXPEDT Version MS-DOS     |
                  | A menu driven routine to edit .EXP files |
                  | Distributed on 28/ 6/2000; 0:34:42       |
                  |------------------------------------------|

        |---------------------------------------------------------------|
        |             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  1 CAD4RD  MS-DOS 2000-07-08T10:19:37

Is this the file you wish to use? (<?>,K,Q,R,Y) >
```

To make a copy of this experiment file and commence editing enter ëYí. If you are brave you can use the ëKí option that skips the copy operation. Be aware that if you mess up the edit you will have to live with it because the ëQíuit option is not available when the ëKíeep option is selected.

```
Experiment title:
         Single Crystal Exercise
The last history record is :
    HSTRY  1 CAD4RD  MS-DOS 2000-07-08T10:19:37

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 ëSí.

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

You should look at this menu further, so enter ë↵í 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 ëAí.

```
The absorption flag is                    NONE
The radiation type flag is                MoKa
The absorption coefficient is        .000
The maximum value of d* to be used is  2.000
The instrument error constant is       .0100
The constant variance term is       .0000
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  .9841   10.0  .9372   20.0  .7982   30.0  .9360   40.0  .9400
  50.0  .8914   60.0  .9389   70.0  .9972   80.0  .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  .8971 -170.0  .9743
-160.0  .8085 -150.0  .8720 -140.0  .8748 -130.0  .8194 -120.0  .8766
-110.0  .9314 -100.0  .9875  -90.0  .8268  -80.0  .9343  -70.0  .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 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 the ψ-scan data is listed. Another new menu, let us look at it by typing ë?í.

```
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 and ψ-scan data. Enter ëWí 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 ë0.15í to define the radius of the sphere.

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

No, don't modify the ψ scan data, so enter either ëNí or ë↵í.

```
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 ëXí to exit.

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

Enter ëXí to exit from SCABS control editing.

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

Enter ëXí 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 ëXí to exit from EXPEDT.

```
EXPEDT terminated successfully
```

Now you are ready to perform the absorption calculations. Enter ëscabsí for Unix or select ëScabsí in the ëComputeí pull down window in Windows to perform the absorption calculations. This job will complete in a few seconds and the output is sent to the list file. When it finishes you are ready for the next step. The following will appear.

```
Histogram  1  KENT'S H3O+SBF5- LOW TEMP -50C       173 4.0 1.3 5.9

<Sig(I)>/<I>     =   .0212
<Sig(FSQ)>/<FSQ> =   .0314
<Sig(F)>/<F>     =   .2449
SCABS completed successfully
```

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$\bar{3}$ and it is of interest to check the intensity of the various parity classes to determine the correct space group. Enter ëistatsí at the GSAS prompt for Unix or select ëIstatsí in the ëResultsí pull down menu for Windows. The following output will appear on both the screen and the list file. We have marked by asterisks the reflection classes that should be extinct for Ib3 in the manual. They will not in either the screen output or the list file.

```
               |-----------------------------------------------|
               |        Program ISTATS Version MS-DOS          |
               | Program for determining reflection statistics |
               |    Distributed on 28/ 6/2000; 0:36:44         |
               |-----------------------------------------------|

       |----------------------------------------------------------------|
       |             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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       |----------------------------------------------------------------|

 Histogram 1 has  1460 reflections

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  *
Stop - Program terminated.
```

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

The next step is to merge the equivalent reflections to give the unique set for the space group Ib3. For Unix enter ëscmergeí or select ëScmergeí from the ëComputeí pull down menu for Windows. A summary of the reflection merge will appear.

```
IHIST   REF.

  147 Reflections were averaged over  1 data sets
  173 Reflections were averaged over  2 data sets
   47 Reflections were averaged over  3 data sets

         R Factor based on F    =      803.991/    15598.360 =  .0515
Weighted R factor based on F    =     2131.652/    46074.380 =  .0463

         R Factor based on Fsqd =   108130.600/  1194662.000 =  .0905
Weighted R factor based on Fsqd =       42.473/      322.361 =  .1318
SCMERGE completed
```

Patterson Calculations

Next you need to generate a Patterson map so that you can solve the structure from the set of vectors. Thus, the first step here is to enter ëexpedtí (or select ëExpedtí) for the Fourier setup of a Patterson map.

```
                 |------------------------------------------|
                 |       Program EXPEDT Version MS-DOS      |
                 | A menu driven routine to edit .EXP files |
                 | Distributed on 28/ 6/2000; 0:34:42       |
                 |------------------------------------------|

       |---------------------------------------------------------------|
       |           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  3 SCABS   MS-DOS 2000-07-08T11:09:04  Finished

Is this the file you wish to use? (<?>,K,Q,R,Y) >
```

To start editing Fourier controls enter ëK Fí. The current experiment file will be opened for editing.

```
Experiment title:
         Single Crystal Exercise
The last history record is :
    HSTRY  3 SCABS   MS-DOS 2000-07-08T11:09:04  Finished

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

You want to calculate a Patterson map, enter ëptsní. 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 ëXí.

```
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 ë↵í.

```
Current overall map step size is   .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 ë0.1í.

```
The a-axis is  10.139970 A
The new del-x is   .1014 A
The cell will be divided into  100 points along x
The b-axis is  10.139970 A
The new del-y is   .1014 A
The cell will be divided into  100 points along y
The c-axis is  10.139970 A
The new del-z is   .1014 A
The cell will be divided into  100 points along z
Old x limits are   .0000 to   .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 ëInternational Tables for X-ray Crystallography Vol. Aí for this space group suggest that you should enter the limits ë0 1/4 0 1/4 0 1/2í.

```
New x limits are   .0000 to   .2500
Old y limits are   .0000 to   .0000
New y limits are   .0000 to   .2500
Old z limits are   .0000 to   .0000
New z limits are   .0000 to   .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 ë1 0í to include it and terminate the list.

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

You are all done entering the Fourier controls so enter ëXí.

```
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 ëXí to exit.

```
EXPEDT terminated successfully
```

Then enter ëfourierí for Unix or select ëFourierí for Windows and the following summary of the Patterson map calculations will appear.

```
Calculation of a PTSN map was requested.
CPU time for reading reflections was        .06 sec.
CPU time for this FOURIER map was        .05 sec.
FOURIER completed successfully
```

After this you will be ready for the map search step.

Map Search and Structure Solution

Next you will need to determine the location of peaks in the Patterson map. The program FORSRH will do this for you, so at the Unix GSAS prompt enter ëforsrhí or select ëForsrhí from the ëComputeí pull down menu in Windows and you will get the following screen.

```
                   |------------------------------------------|
                   |      Program FORSRH Version MS-DOS       |
                   |     Fourier map peak search program      |
                   | Distributed on 28/ 6/2000; 0:35:24       |
                   |------------------------------------------|

        |---------------------------------------------------------------|
        |            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 -235.257 to 9295.910
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 ë50í 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 ë50í 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 ëNí 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? N

The following vectors were found
          Rho       X       Y       Z         Length
   1    9295.910   .0000   .0000   .0000         .00
   2    8546.374   .0000   .5000   .0000        5.07
   3    1236.022   .2500   .2500   .2500        4.39
   4     325.742   .0597   .3626   .3982        5.49
   5     296.719   .0611   .3648   .1023        3.89
   6     295.832   .0616   .1352   .1034        1.84
   7     289.289   .0618   .1353   .3967        4.30
Total CPU time for FORSRH was    .17 seconds
FORSRH terminated successfully.
```

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 of m3m symmetry 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 FORPLOT 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. Peak number 6 is about the right length (1.84) 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 -0.0616,0.1352,0.1034.

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 the 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 ëexpedtí at the Unix GSAS prompt or select ëExpedtí in Windows; the following familiar screen will appear.

```
                  |------------------------------------------|
                  |        Program EXPEDT Version MS-DOS      |
                  | A menu driven routine to edit .EXP files |
                  | Distributed on 28/ 6/2000; 0:34:42       |
                  |------------------------------------------|

        |---------------------------------------------------------------|
        |           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  5 SCMERGE MS-DOS 2000-07-08T11:31:25

Is this the file you wish to use? (<?>,K,Q,R,Y) >
```

The first steps are to open this experiment file, enter least-squares editing and then atom editing. Enter ëK L Aí to get there.

```
Experiment title:
         Single Crystal Exercise
The last history record is :
    HSTRY  5 SCMERGE MS-DOS 2000-07-08T11:31:25

Phase No. 1; Phase has      0 atoms; 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 $(H_3O)^+(SbF_6)^-$. Start by entering ëI 1í.

```
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 ëSB 0 0 0 1 / I /í. 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    .00000  .00000  .00000 1.00000 SB1       .02500 I     -3(111)  8 000
Phase No. 1; Phase has      1 atoms; 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 ëI N O 1/4 1/4 1/4 1 / I /í, again don't worry about the line wrap.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM MULT FXU
  2 O     .25000  .25000  .25000 1.00000 O2        .02500 I     -3(111)  8 000
Phase No. 1; Phase has      2 atoms; 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 ëI N F -0.0616 0.1352 0.1034 1 / I /í. 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    -.06160  .13520  .10340 1.00000 F3        .02500 I        1    48 000
Phase No. 1; Phase has      3 atoms; 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 ëV 1:3 X Uí. This sets the flags for all three atoms.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM MULT FXU
  1 SB    .00000  .00000  .00000 1.00000 SB1       .02500 I XU  -3(111)  8 000
  2 O     .25000  .25000  .25000 1.00000 O2        .02500 I XU  -3(111)  8 000
  3 F    -.06160  .13520  .10340 1.00000 F3        .02500 I XU     1    48 000
Phase No. 1; Phase has      3 atoms; 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, now enter ëXí.

```
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 ëLí 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   .000
Maximum D-spacing is 99.990
Include all data as observed
Enter L-S control editing option (<?>,A,B,C,D,F,G,I,J,K,L,M,N,P,S,V,W,X)
```

You are told the defaults for single crystal refinements. Enter ë↵í to see the help listing.

```
 A a - Maximum atom position shift
 B b - Matrix band width (0 full matrix)
 C n - Maximum number of cycles
 D d - Marquardt factor
 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
 V n - Convergence criterion
 W n - Refinement weight option "n"
 X   - Exit from editing least squares controls
Enter L-S control editing option (<?>,A,B,C,D,F,G,I,J,K,L,M,N,P,S,V,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 ëC 5 S 1.5 F N Xí. 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 ëO H C 0.4 X X Xí. Some messages will appear as the scale is changed. You need not set the refinement flag, it is set ëYí by default.

```
Editing histogram scale factors
Histogram no.   1
Title: KENT'S H3O+SBF5- LOW TEMP -50C       173 4.0 1.3 5.9
**** Histogram will be used in least-squares

Histo. scale =      1.0000     Refine Y Damping flag =  0
Histogram no.   1
Title: KENT'S H3O+SBF5- LOW TEMP -50C       173 4.0 1.3 5.9
**** Histogram will be used in least-squares

Histo. scale =      .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 ëXí on a new line. Do that now.

```
EXPEDT terminated successfully
```

The atoms are entered and the least squares controls are now set. Enter ëgenlesí at the Unix GSAS prompt or select ëGenlesí from the Windows ëComputeí pull down menu and respond to the log file and queue questions. The run will take a few seconds; when it finishes you can examine the results in the list file. The output on the screen will mostly scroll up out of view. Here are the results from the last cycle of least squares.

```
Restraint data statistics:
 Cycle   4 There were   259 observations. Total before-cycle CHI**2 =1.1227E+04

Reduced CHI**2 =  44.55     for     7 variables

The single crystal function minimized is CHI**2 = w*(Fo-Fc)**2

Histogram  1  Type SXC   Nobs=  259    R(F) =   .0836  CHI**2= 1.1227E+04

Single crystal Rw(Fo) =   .075 for   259 observations

Final variable sum((shift/esd)**2) for cycle   4:        .00 Time:     .22 sec

Convergence was achieved and
GENLES terminated successfully
```

The refinement converged quite rapidly and required only 4 cycles to complete. GENLES senses that convergence was achieved before the requested 5 cycles and so terminated the run.

Anisotropic Refinement and Structure Results

After GENLES finishes and you have satisfied yourself that all is going well it 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 ëexpedtí at the Unix GSAS prompt or select ëExpedtí for Windows.

```
                  |------------------------------------------|
                  |        Program EXPEDT Version MS-DOS      |
                  | A menu driven routine to edit .EXP files |
                  | Distributed on 28/ 6/2000; 0:34:42        |
                  |------------------------------------------|

        |----------------------------------------------------------------|
        |            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, 2000, The Regents of the University of California. |
        |----------------------------------------------------------------|

The last history record is :
    HSTRY  7 GENLES  MS-DOS 2000-07-08T12:03:21  Sdsq=  .112E+05 S/E=  .119E-03

Is this the file you wish to use? (<?>,D,K,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 ëK L A Lí to do all of these.

```
Experiment title:
         Single Crystal Exercise
The last history record is :
    HSTRY  7 GENLES  MS-DOS 2000-07-08T12:03:21  Sdsq=  .112E+05 S/E=  .119E-03

Phase No. 1; Phase has      3 atoms; Title: (H3O)+(SbF6)-
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM MULT FXU
  1 SB    .00000  .00000  .00000 1.00000 SB1       .01520 I XU  -3(111)  8 000
  2 O     .25000  .25000  .25000 1.00000 O2        .03685 I XU  -3(111)  8 000
  3 F   -.05996  .14048  .10431 1.00000 F3        .02622 I XU     1    48 000
Phase No. 1; Phase has      3 atoms; 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 ëU 1:3 A X X Xí.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM MULT FXU
  1 SB    .00000  .00000  .00000 1.00000 SB1              A XU  -3(111)  8 000
U11,U22,U33,U12,U13,U23 =   .01520   .01520   .01520   .00000   .00000   .00000
  2 O     .25000  .25000  .25000 1.00000 O2               A XU  -3(111)  8 000
U11,U22,U33,U12,U13,U23 =   .03685   .03685   .03685   .00000   .00000   .00000
  3 F   -.05996  .14048  .10431 1.00000 F3               A XU     1    48 000
U11,U22,U33,U12,U13,U23 =   .02622   .02622   .02622   .00000   .00000   .00000
Phase No. 1; Phase has      3 atoms; 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 are listed and then the last menu in EXPEDT is shown. To exit from this one you must enter ëXí on a new line, do this now.

```
EXPEDT terminated successfully
```

To finish the refinement and calculate some structural results enter ëgenlesí then ëdisaglí and then ëbijcalcí (for Unix systems). Each will display a summary of its results as they finish. In Windows select ëGenlesí (in ëComputeí), ëDisaglí (in ëResultsí) and ëBijcalcí (also in ëResultsí) waiting for each to finish before selecting the next one. The results of these calculations can be found in your list file. The results from the last cycle in GENLES are shown.

```
Restraint data statistics:
 Cycle   9 There were   259 observations. Total before-cycle CHI**2 =6.1118E+03

Reduced CHI**2 =  24.95     for    14 variables

The single crystal function minimized is CHI**2 = w*(Fo-Fc)**2

Histogram  1  Type SXC   Nobs=  259    R(F) =   .0610  CHI**2= 6.1118E+03

Single crystal Rw(Fo) =   .056 for   259 observations

Final variable sum((shift/esd)**2) for cycle   9:        .00 Time:     .22 sec

Convergence was achieved and
GENLES terminated successfully
```

Then the results from DISAGL are next. This shows nothing other than it finished; the real results are in the OXON.LST file

```
DISAGL successful completion
```

Finally the results from BIJCALC are shown. This summarizes the results giving the equivalent isotropic thermal parameters for each atom.

```
Atom SB1       100*Ueqv =   1.55
Atom O2        100*Ueqv =   3.83
Atom F3        100*Ueqv =   2.94
Stop - Program terminated.
```

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 ëortepí at the Unix GSAS prompt or select ëOrtepí in the ëGraphicsí pull down menu in Windows.

```
           |----------------------------------------------------|
           |              Program ORTEP Version MS-DOS          |
           | Crystal structure plotting program by C.K. Johnson |
           |      Distributed on 28/ 6/2000; 0:36:56            |
           |----------------------------------------------------|

      |---------------------------------------------------------------|
      |           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, 2000, The Regents of the University of California. |
      |---------------------------------------------------------------|

Enter graphic screen option (<?>,A,B,Z) >
```

As usual for this question enter your terminal type and an ëNí 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 internally and add extra atoms as necessary to give 96 operators.

```
Title: Single Crystal Exercise
Phase name: (H3O)+(SbF6)-
Lattice parameters:
a,b,c            =    10.1400   10.1400   10.1400
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

Enter <CR> to continue >
```

Enter ë↵í to see the remaining listing. 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.

```
Atomic coordinates (Uij*100):
ser.   x       y       z     name      U11    U22    U33    U12    U13    U23
  1   .0000   .0000   .0000 SB1        1.55   1.55   1.55    .44    .44    .44
  2   .2500   .2500   .2500 O2         3.83   3.83   3.83   1.58   1.58   1.58
  3  -.0589   .1409   .1042 F3         3.70   2.33   2.78    .42   1.02   -.43
  4   .0000   .0000   .0000 ORIGIN      .05    .00    .00    .00    .00    .00
  5   .5000   .5000   .5000 CENTER      .05    .00    .00    .00    .00    .00
New crystal to cartesian transformation matrix:
    .09862    .00000    .00000
    .00000    .09862    .00000
    .00000    .00000    .09862
No atoms in drawing array
Atom names:
  1 SB1        2 O2         3 F3         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 ë↵í 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 ë↵í to continue.

```
Atom names:
  1 SB1        2 O2         3 F3         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 ëAí 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 ë155501í.

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

That is the only atom you want to select that way, enter ë0í 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 ëSí 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 ë155501í 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 ë155501í.

```
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 ë3í.

```
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 ë3í 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 2 , however there is a ìbugî in this part of ORTEP for GSAS that needs a larger value, so enter ë3.0í. ORTEP will find all atom number 3's that fall within 3 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 ëLí.

```
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 have the same unit cell designator (555), the symmetry operators for the atoms selected might have been difficult to determine manually. You are finished here so enter ëXí. 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 (<?>,A,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 ë↵í to see the help listing.

```
ORTEP commands:
 <?>   - Type this help listing
 A     - Change atom colors
 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 (<?>,A,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 ëBí 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 ë↵í 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 ëIí 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 ë1í 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 ë1í.

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

Next you have to select the range of target atoms for the bond drawing. Enter ë3í so that the bonds are drawn to the F atoms.

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

Again the target atom list must be terminated, enter ë3í.

```
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 ë3í 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 ë1 2 0.02í to draw bonds 0.04 thick between 1.0 and 2.0 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. ë1 1 3 3 3 1 2 0.02í).

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

To see the bond drawing control you have entered, type ëLí.

```
Bond selection controls:
No.  Ori. ANR  Tar. ANR  Type    D-min   D-max   Radius
    1    1    1    3    3    3  1.0000  2.0000   .0200
Atom names:
  1 SB1         2 O2          3 F3          4 ORIGIN      5 CENTER
Enter bond selection command (<?>,D,I,L,X) >
```

This is the only bond control needed so enter ëXí to leave this menu. ORTEP writes this information on the experiment file.

```
Enter ORTEP command (<?>,A,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 ëCí command.

```
Do you want the best view of the model (<Y>/N)? >
```

Respond with a ë↵í, a best view through the ion is selected for drawing. After this command is done then any of the other positioning commands (ëRí or ëVí) 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 ëEí.

```
Enter ellipsoid style (<?>,A,B,C,D) and scale >
```

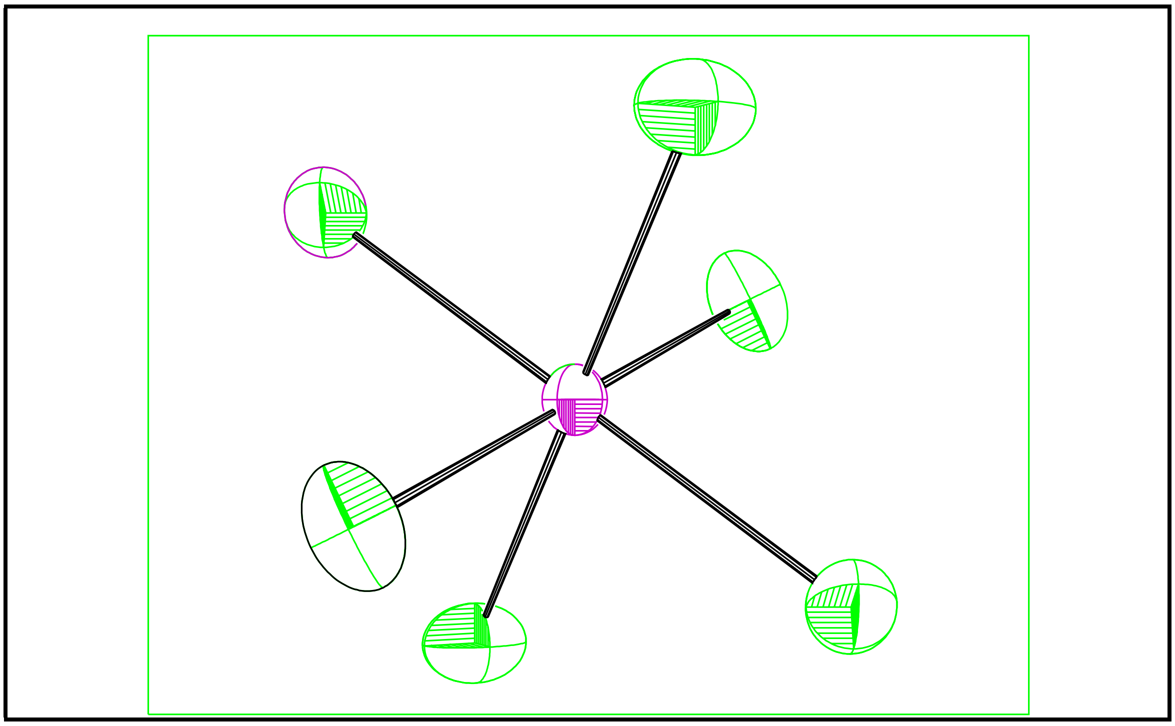
You may enter ë↵í to see the help listing here, the ëAí option displays the ellipsoids in the cross-hatched octant style so commonly seen in crystallographic publications.

```
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 ë/í.

```
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 ëPí and the plot will immediately follow.



As usual enter ë↵í to get the next prompt.

```
Enter ORTEP command (<?>,A,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 (ëTí command) especially the cursor-controlled atom-labeling feature. To exit from ORTEP enter ëQí.

```
ORTEP has finished
```

This completes the fourth exercise. Many of the GSAS programs used in this exercise wrote information to a list file. You should examine it with the Unix GSAS utilities ELST, TLST and SLST or any Windows text editor.

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_{ph}, 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

$F_{ph} = A_{ph} + iB_{ph}$

where A and B are the real and imaginary 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 the atomic site fraction (x) and the thermal motion correction (Tî - see below)

f = xTî(f_o + fí + ifî)

the expressions for A and B are then broken down into three components each

A = A_o + Aí - Bî

B = B_o + Bí + Aî

where

$$A_O = \sum_i x_i T''_i f_{oi} \, cos\, 2\pi h \cdot r \qquad B_O = \sum_i x_i T''_i f_{oi} \, sin\, 2\pi h \cdot r$$

$$Aí = \sum_i x_i T''_i f'_i \, cos\, 2\pi h \cdot r \qquad Bí = \sum_i x_i T''_i f'_i \, sin\, 2\pi h \cdot r$$

$$Aî = \sum_i x_i T''_i f''_i \, cos\, 2\pi h \cdot r \qquad Bî = \sum_i x_i T''_i f''_i \, sin\, 2\pi h \cdot r$$

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 = xTî(b_o +bí+ ibî)

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 compared to the single crystal case to represent the powder intensity

$$F^2 = (A_o+\text{Aí})^2 + \text{Bî}^2 + (B_o+\text{Bí})^2 + \text{Aî}^2$$

In GSAS the atomic coordinates, site fractions and thermal motion parameters are refinable quantities. In addition, the anomalous dispersion contributions (fí and fî) 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

$$\text{Tî} = e\ -(8\pi^2 U_{iso} \sin^2 \Theta/\lambda^2)$$

for isotropic thermal motion or

$$\text{Tî} = e\ -[2\pi^2 (u_{11} h^2 a^{*2} + \ldots + 2u_{12} hka^* b^* + \ldots)]$$

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.

X-ray scattering factors are calculated in GSAS from the appropriate coefficients for the function

$$f_o = c + \sum_{i=1}^{4} a_i\, exp\left(-b_i\, sin^2 \Theta / \lambda^2\right)$$

and the coefficients for this function are those given by Cromer & Waber, International Tables for X-ray Crystallography, Vol. IV (1971). These for every element and usual ion to ^{98}Cf are stored in the file /gsas/data/atmdata.dat. The anomalous x-ray scattering coefficients, fí and fî, for these elements used in GSAS are those of Cromer, International Tables for X-ray Crystallography, Vol. IV (1971) and are stored in the same file for use by GSAS.

Neutron scattering lengths listed by Koster & Yelon, Neutron Diffraction Newsletter (1982) are given in the file /gsas/data/atmdata.dat for all the atoms and commonly occurring isotopes. In a few cases the real and imaginary neutron scattering lengths are computed from an empirical fit with a modified Breit-Wigner function to data tabulated by Lynn & Seeger, Atomic Data and Nuclear Data Tables, 44, 191-207 (1990). The functions used are

$$b' = b_1\left[\frac{E-b_3}{(E-b_3)^2-b_4^2}+\frac{b_5(E-b_6)}{(E-b_6)^2-b_4^2}+\frac{b_7(E-b_8)}{(E-b_8)^2-b_4^2}\right]$$

$$b'' = -b_2\left[\frac{1}{(E-b_3)^2-b_4^2}+\frac{b_5}{(E-b_6)^2-b_4^2}+\frac{b_7}{(E-b_8)^2-b_4^2}\right]$$

given that the neutron energy is

$$E = {81.80703}/{\lambda^2}$$

The coefficients, b_1-b_8, for these equations are stored for selected elements and isotopes in the file /gsas/data/atmdata.dat for use by GSAS.

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

$$F_{mag} = \sum_i q_i p_i e^{2\pi i h \cdot x_i}$$

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 F_{mag}. The magnetic scattering length is a function of the magnitude of the magnetic moment (S) and the magnetic form factor (f_m) for the magnetic atom

$$p = 0.54Sf_m \text{ x } 10^{-12} \text{ cm}$$

and the magnetic interaction vector for the j^{th} atom depends on the unit vector ($\boldsymbol{\varepsilon}$) for the scattering vector (h) and the unit vector for the magnetic moment on that atom(K_j)

$$q_j = \boldsymbol{\varepsilon}(\boldsymbol{\varepsilon}\cdot K_j)-K_j$$

Magnetic structure factors and derivatives are calculated in MAGSTRFCTR.

The magnetic form factors in GSAS are computed in a way similar to that for the x-ray form factors.

$$f_m = C + \sum_{i=1}^{4} A_i \, exp\left(-B_i \, sin^2\Theta/\lambda^2\right) + \left(1-\frac{g}{2}\right)\left[C' + \sum_{i=1}^{4} A'_i \, exp\left(-B'_i \, sin^2\Theta/\lambda^2\right)\right]$$

where the coefficients A_i, B_i and C are for the <j0> form factor and Aí$_i$, Bí$_i$ and Cí are for the <j2> form factor as given in the International Tables for Crystallography, Vol. C

(1992) for a selected set of elements and ions. The LandÈ g factor depends on the expected spin-orbit coupling for the particular atomic species. Typically g=2 for 1st row transition elements in high oxidation states and less for other elements and ions.

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.

Solvent Scattering Factor

The effect of scattering from the solvent molecules that are present in macromolecular structures can be accounted by use of ìBabinetís Principleî in which the atomic scattering factors, f_o, are modified by

$$f = f_o - A\,exp\left(\frac{-8\pi^2 U\,sin^2\Theta}{\lambda^2}\right)$$

The coefficients A and U are refinable in GSAS; typical values are A=3-6 and U=1-10. Solvent scattering corrections are edited in EDTSOLV for EXPEDT. Input and output of these corrections in GENLES are done by FSOVINP and FSOVOUT; the calculation of the correction is done in STRFCTR.

Single Crystal Extinction

In the case of single crystal diffraction data an extinction correction is available. Primary and both type I and type II secondary extinction models are considered in either the Gaussian or Lorentzian forms. The correction in GSAS is applied to F_c^2 as $Fí_c^2=F_c^2/E_h$ which is compared to F_o^2 in the refinement.

For the Gaussian approximation

$$E_h = \sqrt{1 + 2x + \frac{(0.58 + 0.48\,cos\,2\Theta + 0.24\,cos^2\,2\Theta)x^2}{1 + (0.02 - 0.025\,cos\,2\Theta)x}}$$

and for the Lorentzian approximation

$$E_h = \sqrt{1 + 2x + \frac{(0.025 + 0.285\,cos\,2\Theta)x^2}{1 + 0.15x - 0.2(0.75 - cos\,2\Theta)^2\,x}}$$

for 2Θ<90 or

$$E_h = \sqrt{1 + 2x + \frac{(0.025 + 0.285\,cos\,2\Theta)x^2}{1 - 0.45(x)cos\,2\Theta}}$$

for 2Θ>90 .

The extinction factor, x, depends on the type of extinction. For secondary type I extinction

$$x = \frac{7.9406x10^5 \lambda^3 F_c^2 \bar{t} E_g \left(\cos 2\Theta_m + \cos^4 2\Theta\right)}{V_o^2 \sin 2\Theta \left(\cos 2\Theta_m + \cos^2 2\Theta\right)} \text{ for x-rays, and}$$

$$x = \frac{1.0x10^7 \lambda^3 F_c^2 \bar{t} E_g}{V_o^2 \sin 2\Theta} \text{ for CW neutrons, and}$$

$$x = \frac{1.0x10^7 \lambda^4 F_c^2 \bar{t} E_g}{V_o^2 \sin^2 \Theta} \text{ for TOF neutrons.}$$

For secondary type II extinction

$$x = \frac{7.9406x10^5 \lambda^2 F_c^2 \bar{t} E_s \left(\cos 2\Theta_m + \cos^4 2\Theta\right)}{V_o^2 \left(\cos 2\Theta_m + \cos^2 2\Theta\right)} \text{ for x-rays, and}$$

$$x = \frac{1.0x10^7 \lambda^2 F_c^2 \bar{t} E_s}{V_o^2} \text{ for neutrons.}$$

For combined secondary types I and II extinction

$$x = \frac{7.9406x10^5 \lambda^2 F_c^2 \bar{t} E_g \left(\cos 2\Theta_m + \cos^4 2\Theta\right)}{V_o^2 \left(\cos 2\Theta_m + \cos^2 2\Theta\right)\sqrt{1 + \frac{E_s \sin 2\Theta}{\lambda E_g^2}}} \text{ for x-rays, and}$$

$$x = \frac{1.0x10^7 \lambda^2 F_c^2 \bar{t} E_g}{V_o^2 \sqrt{1 + \frac{E_s \sin 2\Theta}{\lambda E_g^2}}} \text{ for CW neutrons, and}$$

$$x = \frac{1.0x10^7 \lambda^2 F_c^2 \bar{t} E_g}{V_o^2 \sqrt{1 + \frac{E_s \sin^2 \Theta}{\lambda^2 E_g^2}}} \text{ for TOF neutrons.}$$

For primary extinction

$$x = \frac{7.9406x10^5 \frac{3}{2} \lambda^2 F_c^2 E_p \left(\cos 2\Theta_m + \cos^4 2\Theta\right)}{V_o^2 \left(\cos 2\Theta_m + \cos^2 2\Theta\right)} \text{ for x-rays, and}$$

$$x = \frac{1.0x10^7 \frac{3}{2} \lambda^2 F_c^2 E_p}{V_o^2} \text{ for neutrons.}$$

The mean path of the radiation through the crystal for the given hkl is $\bar{t}$ and the values available for refinement are Eg, Es and Ep. These are edited in EDTSEXT, input and output in GENLES by EXTSINP and EXTSOUT. Calculations are done in EXTSCAL.

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, I_b, is modeled with a well-behaved empirical function. A diffuse scattering contribution, I_d, can also be included. 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

$$I_c = I_b + I_d + S_h \sum_p S_{ph} Y_{ph}$$

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_{ph} is the individual phase scale factor within an histogram and Y_{ph} 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. 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 (esdís) 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 ëITYP 1í function is a sum of exponentials of TOF (T) in milliseconds or 2Θ in degrees.

$$I_i = P_1 + P_2\, exp\left[-P_3 T\right] + P_4\, exp\left[-P_5 T^2\right] + !$$

This function has a maximum of 11 coefficients.

The ëITYP 2í 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.

$$I_i = P_1 + \frac{P_2}{T^5} exp\left[-P_3 / T^2\right] + P_4\, exp\left[-P_5 T^2\right] + !$$

Again there is a maximum of 11 coefficients. The coefficient P_3 in this function and the ëITYP 4í function shown below can be used to calculate an effective moderator temperature by

$$t = \frac{2.374x10^{-4} C^2}{P_3\, sin\, 2\Theta}$$

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 ëITYP 3í function is a 12 term Chebyschev polynomial of the first kind (ìHandbook of Mathematical Functions,î M. Abramowitz and I.A. Stegun, Eds., Ch. 22).

$$I_i = \sum_{j=1}^{N} P_j T'_{j-1}$$

where $Tí_{j-1}$ 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 that is the orthogonal range for this function.

The ëITYP 4í incident intensity function has a Maxwellian term and part of the Chebyschev polynomial used for ëTYPE 3í. It is not used for x-rays.

$$I_i = P_1 + \frac{P_2}{T^5} exp\left[-P_3/T^2\right] + \sum_{j=4}^{N} P_j T'_{j-3}$$

Again T is TOF in milliseconds and Tíi are the coefficients of the Chebyschev polynomial of the first kind.

The ëITYP 5í function is the same as ëTYPE 3í except that X is defined as

X = T/10

The ëITYP 3í, ëITYP 4í and ëITYP 5í functions have a maximum of 12 coefficients.

For constant wavelength data with no incident spectrum, a ëITYP 0í incident spectrum is used and has no coefficients; this gives I_i = 1.0 for all data points and σI_o is dependent only on I_o.

Alternatively, one can use a point-by-point measured incident spectrum, ëITYP10í, instead of the fitted one; the file containing this spectrum is read along with the corresponding powder pattern by routine HSTREAD in POWPREF. 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 nine background functions available in GSAS for fitting to powder diffraction data. Each function has a maximum of 36 possible coefficients although in virtually 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 ëChebyschev polynomial of the first kindí and is similar to that used for the incident spectrum ëTYPE 3í. 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

$$I_b = \sum_{j=1}^{N} B_j T'_{j-1}$$

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.

$$I_b = B_1 + \sum_{j=2}^{N} B_j \, cos\left[P * (j-1)\right]$$

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 (Debye scattering) 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

$$I_b = B_1 + B_2 T + \sum_{i=1}^{N-2} \frac{B_{2i+1} \, sin(QB_{2i+2})}{QB_{2i+2}}$$

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. Obviously, the number of terms is always an even number for this function.

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

$$I_b = \sum_{j=1}^{N} B_j \frac{Q^{2(j-1)}}{(j-1)!}$$

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

$$I_b = \sum_{j=1}^{N} B_j \frac{(j-1)!}{Q^{2(j-1)}}$$

The sixth function is then a mixing of the previous two functions that can account for the background contributions at both low Q and high Q.

$$I_b = B_1 + \sum_{j=1}^{N}\left(B_{2j}\frac{Q^{2j}}{j!} + B_{2j+1}\frac{j!}{Q^{2j}} \right)$$

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. The number of terms may be either even or odd for this function. All three of these latter functions use the same definition for Q that is used for the third function.

The seventh function uses a simple linear interpolation formula for the background. The chosen number of terms is used to partition the powder scan range into N-1 equal segments in T (TOF or 2Θ). For a point within a particular segment the background is calculated by

$$I_b = B_j\left(T_{j+1} - T\right) + B_{j+1}\left(T - T_j\right) \text{ for } T_j \le T \le T_{j+1}.$$

The B_j are adjustable parameters in the least squares but the locations (T_j) are fixed. This function will fit almost any background variation quite readily. Use of a very large number of terms is risky, as the background function will begin to fit up under the Bragg peaks.

The eighth function is essentially identical to the seventh function except that the powder profile scan is partitioned into equal segments in 1/T. This concentrates the intervals at the small d-spacing region of the powder pattern where changes in the level of the background are more likely to occur. Otherwise the operation of this background function is identical to the seventh one.

The ninth function is an extension of function three and has a simple polynomial fit for the ìtrueî background and then a sequence of modified Debye terms for fitting contributions from diffuse scattering. The true background is of the form

$$I_{bt} = \sum_{j=1}^{N} B_j \frac{Q^{2(j-1)}}{(j-1)!}$$

This is the same function as background function four and is intended to model background contribution from thermal diffuse scattering; up to 5 terms of this function are allowed to be used.

The remaining terms of background function nine are selected from three possible choices. Each choice has three coefficients for each term. The coefficients are amplitude, interatomic radius and a thermal motion coefficient. The first choice is a modification of the Debye terms used in background function three that includes the thermal motion correction

$$I_{b1} = B_j \frac{\mathit{sin}\left(QB_{j+1}\right)}{QB_{j+1}} \mathit{exp}\left(-\tfrac{1}{2}B_{j+2}Q^2\right)$$

and can be ascribed to the diffuse scattering caused by substitutional disorder.

The second choice is the first derivative of the modified Debye term

$$I_{b2} = B_j \frac{QB_{j+1} \mathit{cos}(QB_{j+1}) - \mathit{sin}(QB_{j+1})}{QB_{j+1}^2} \mathit{exp}\left(-\tfrac{1}{2}B_{j+2}Q^2\right)$$

and can be ascribed to the diffuse scattering caused by positional disorder.

The third choice is the second derivative

$$I_{b3} = B_j \frac{Q^2B_{j+1}^2 \mathit{sin}(QB_{j+1}) + 2QB_{j+1} \mathit{cos}(QB_{j+1}) - 2\,\mathit{sin}(QB_{j+1})}{QB_{j+1}^3} \mathit{exp}\left(-\tfrac{1}{2}B_{j+2}Q^2\right)$$

and can be ascribed to the diffuse scattering caused by vibrational correlation.

The background computed for this function is then the sum of these pieces

$I_b = I_{bt}+\Sigma I_{b1}+\Sigma I_{b2}+\Sigma I_{b3}$

Except for functions #3 and #9, 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.

Diffuse Scattering Function

The functions used to describe the diffuse scattering for the ninth background function are also available as a separate diffuse scattering model in GSAS. Consequently the ìtrueî background can be modeled with any of the available functions and a larger number of diffuse scattering terms can be included in the model. As above there is a choice of three different diffuse scattering terms which are the Debye term with thermal motion correction and the first and second derivatives of this function with respect to interatomic distance

$$I_b = B_i \frac{\mathit{sin}(QB_{i+1})}{QB_{i+1}} \mathit{exp}\left(-\tfrac{1}{2}B_{i+2}Q^2\right)$$

$$I_b = B_i \frac{QB_{i+1} \, cos(QB_{i+1}) - sin(QB_{i+1})}{QB_{i+1}^2} exp\left(-\tfrac{1}{2} B_{i+2} Q^2\right)$$

$$I_b = B_i \frac{Q^2 B_{i+1}^2 \, sin(QB_{i+1}) + 2QB_{i+1} \, cos(QB_{i+1}) - 2\, sin(QB_{i+1})}{QB_{i+1}^3} exp\left(-\tfrac{1}{2} B_{i+2} Q^2\right)$$

These can be ascribed to atom substitutional disorter, positional disorder and correlated thermal motion, respectively. Editing of the diffuse scattering coefficients is done in subroutine EDTDIFUS. Input, output and calculations for diffuse scattering for GENLES are done if DIFSINP, DIFSOUT and DIFSCAL, respectively.

Scale Factors – S_h and S_{ph}

There are two types of scale factors for powder diffraction data. The histogram scale, S_h, is applied to reflections from all phases in the sample and the phase fraction scale, S_{ph}, is applied only to reflections from the p-th phase. These latter scales can be used for quantitative phase analysis for powder mixtures. The intensity correction factors, K_{ph}, given below are defined so that the S_{ph} scale factors are proportional to the unit cell composition of the sample. They can be converted to other compositions by appropriate means. For example, weight fractions, W_p, are obtained by

$$W_p = \frac{S_{ph} m_p}{\sum_{p=1}^{N_p} S_{ph} m_p}$$

where m_p is the unit cell mass for phase p. The weight fraction for multiphase mixtures are automatically computed during the least-squares refinement in GENLES and are shown in the EXPNAM.LST file as additional output associated with the results for S_{ph}. The unit cell mass, m_p, for each phase is computed from the atom site multiplicites and fractions present for that phase. An esd for each weight fraction is also given. Editing of the histogram scales are done in EDTHSCAL; input and output for GENLES are done by HSCALINP and HSCALOUT. The phase fraction scales, S_{ph}, are edited by EDTSCAL; input and output for GENLES are done by SCALINP and SCALOUT. SCALOUT calculates the weight fractions and outputs these results. SCALCAL applies both sets of scale factors.

Bragg Intensity - Y_{ph}

The contributed intensity, Y_{ph}, 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.

$$Y_{ph} = F_{ph}^2 H(T - T_{ph}) K_{ph}$$

where F_{ph} is the structure factor for a particular reflection, $H(T\text{-}T_{ph})$ is the value of the profile peak shape function for that reflection at a position, T, displaced from its expected position, T_{ph}, and K_{ph} 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 ëwindowí array which is read by PDCALC as the profile points are processed.

Intensity correction factors

The intensity correction factors, K_{ph}, consist of those factors that are dependent on the sample, the instrument geometry, and the type of radiation used.

$$K_{ph} = E_{ph} A_h O_{ph} M_p L \big/ V_p$$

where E_{ph} is an extinction correction, A_h is an absorption correction, O_{ph} 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_{ph} is a combination of Bragg and Laue components

$$E_{ph} = E_b \, sin^2 \Theta + E_l \, cos^2 \Theta$$

where

$$E_b = 1 \big/ \sqrt{1+x}$$

and

$$E_l = 1 - \frac{x}{2} + \frac{x^2}{4} - \frac{5x^3}{48} + ! \quad \text{for } x < 1$$

or

$$E_l = \sqrt{\frac{2}{\pi x}} \left[1 - \frac{1}{8x} - \frac{3}{128x^2} - \frac{15}{1024x^3} - ! \right] \text{ for } x > 1$$

where

$$x = E_x \left(\frac{\lambda F}{V} \right)^2$$

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, $A_B=\mu R/\lambda$, for a cylindrical sample is calculated for powder data according to an empirical formula (N.N. Lobanov & L. alte da Veiga, 6th European Powder Diffraction Conference, Abstract P12-16, Aug. 22-25, 1998 and N.N. Lobanov, private communication). It is assumed for TOF data that the linear absorption of all components in the sample varies with 1/velocity, and it is indistinguishable from multiple scattering effects within the sample. For constant wavelength data the absorption coefficient, A_h, is related to the value for 1 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; it should not be used for Bragg-Brentano or other flat plate geometries. This empirical formula gives a satisfactory fit to absorption from a cylindrical sample for $A_B\lambda=\mu R<30cm^{-1}$. The Lobanov & alte da Veiga function for $A_B\lambda$ $A_B\lambda=\mu R<3cm^{-1}$ is

$$A_h = exp\left[-k_o A_B\lambda - k_1(A_B\lambda)^2 - k_2(A_B\lambda)^3 - k_3(A_B\lambda)^4\right]$$

where

$$k_o = 1.697653$$

$$k_1 = \left(25.99978 - 0.01911\sin^{1/4}\Theta\right)exp(-0.024514\,sin\,\Theta) + 0.109561\,sin^{1/2}\,\Theta - 26.0456$$

$$k_2 = -0.02489 - 0.39499\,sin\,\Theta + 1.219077\,sin^{3/2}\,\Theta - 1.31268\,sin^2\,\Theta$$
$$+ 0.871081\,sin^{5/2}\,\Theta - 0.2327\,sin^3\,\Theta$$

$$k_3 = 0.003045 + 0.018167\,sin\,\Theta - 0.03305\,sin^2\,\Theta$$

This empirical function has an average accuracy of 0.2% with the largest deviation being 0.5% compared to values given in International Tables for X-ray Crystallography, Vol II, pp291-299 (1967).

For $A_B\lambda=\mu R>3cm^{-1}$ the Lobanov & alte da Veiga function is

$$A_h = \frac{k_4 - k_7}{[1 + k_5(A_B\lambda - 3)]^{k_6}} + k_7$$

where

$$k_4 = 0.01433902 + 0.1107504\,sin\,\Theta - 0.0877629\,sin^2\,\Theta + 0.1002088\,sin^3\,\Theta - 0.0336778\,sin^4\,\Theta$$

$$k_5 = (0.013869 - 0.01249\,sin\,\Theta)exp(3.27094\,sin\,\Theta) + \frac{0.337894 + 13.77317\,sin\,\Theta}{(1 + 11.53544\,sin\,\Theta)^{1.555039}}$$

$$k_6 = \frac{1.933433}{(1 + 23.12967\,sin\,\Theta)^{1.686715}} - 0.13576\,sin^{1/2}\,\Theta + 1.163198$$

$$k_7 = 0.00044365 - \frac{0.004259}{(1 + 0.41051\,sin\,\Theta)^{148.4202}}$$

This empirical function has an average accuracy of 0.2% and a maximum deviation of 0.5% for $A_B\lambda=\mu R<10cm^{-1}$ compared to values given in International Tables for X-ray Crystallography, Vol. II.

The second function is a simple linear absorption that is useful for the neutron case where the beam suffers substantial absorption by passing through sample containment vessels, etc.

$$A_h = exp(-A_B\lambda)$$

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 ìnormalizedî form of the function described by Pitschke, Hermann and Mattern (Powder Diffraction, 8,74-83, 1993).

$$A_h = \frac{1 - A_{B1}\left(1/sin\,\Theta - A_{B2}/sin^2\,\Theta \right)}{1 - A_{B1} + A_{B1}A_{B2}}$$

Function four is a normalized form of the empirical function proposed by Suortti (J. Appl. Cryst. 5, 325-331, 1972).

$$A_h = \frac{A_{B1} + (1 - A_{B1})exp\left(-A_{B2}/sin\,\Theta \right)}{A_{B1} + (1 - A_{B1})exp(-A_{B2})}$$

The two surface roughness functions give essentially identical results, however, the Suortti function is better behaved at low (<20 2Θ) scattering angles.

Function five is for a flat plate sample in transmission geometry. The plate normal can be either perpendicular to the diffraction vector or tilted by some fixed angle ϕ in the diffraction plane. If ϕ is zero the correction is

$$A_h = exp\left(-A_B\lambda/cos\,\Theta \right)$$

If ϕ is nonzero then the correction is

$$A_h = \frac{exp\left(\frac{-A_B\lambda}{cos\,\phi\, cos\,\Theta - sin\,\phi\, sin\,\Theta}\right) - exp\left(\frac{-A_B\lambda}{cos\,\phi\, cos\,\Theta + sin\,\phi\, sin\,\Theta}\right)}{-A_B\lambda\left(1-\frac{cos\,\phi\, cos\,\Theta - sin\,\phi\, sin\,\Theta}{cos\,\phi\, cos\,\Theta + sin\,\phi\, sin\,\Theta}\right)}$$

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: March Dollase function

There are two preferred orientation corrections, O_{ph}, available in GSAS. The first 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.

$$O_{ph} = \frac{1}{M_p}\sum_{j=1}^{M_p}\left(R_o^2 cos^2 A_j + \frac{sin^2 A_j}{R_o}\right)^{-3/2}$$

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 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 that is oriented to be parallel to the incident beam (N. Wright, private communication). This function takes on the form

$$O_{ph} = \frac{1}{M_p}\sum_{j=1}^{M_p}\frac{1}{N}\sum_{k=1}^{N}\left(R_o^2 B_{kj}^2 + \frac{1-B_{kj}^2}{R_o}\right)^{-3/2}$$

where $B_{kj} = \mathit{cos}\, A_j\, \mathit{sin}\, \Theta + \mathit{sin}\, \Delta_k\, \mathit{sin}\, A_j\, \mathit{cos}\, \Theta$ and $0 \leq \Delta_k \leq 2\pi$. This formulation is then a numerical integral over all crystallite orientations about the diffraction vector that is offset from the ellipsoid axis by Θ. This function is used when the sample is oriented so that the preferred orientation is aligned with the incident beam, for example, in a high-pressure diamond anvil experiment.

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.

Preferred orientation of powders: spherical harmonics function

The second preferred orientation correction available in GSAS uses the general axis equation as described by Bunge, ìTexture Analysis in Materials Scienceî (1982) and implemented in GSAS by Von Dreele, J. Appl. Cryst., 30, 517-525 (1997). The preferred orientation correction, $O_p(h,y)$, for this formulation depends on both the reflection, h, and on the sample orientation, y. The general axis equation is

$$O_p(h,y) = 1 + \sum_{L=2}^{N_L} \frac{4\pi}{2L+1} \sum_{m=-L}^{L} \sum_{n=-L}^{L} C_L^{mn} k_L^m(h) k_L^n(y)$$

The two harmonic terms, $k_L^m(h)$ and $k_L^n(y)$, take on values according to the crystal and sample symmetries, respectively, and thus the two inner summations are over only the resulting unique, nonzero harmonic terms. These unique terms are automatically selected by GSAS according to the space group symmetry and the user chosen sample symmetry. The available sample symmetries are cylindrical symmetry, 2/m, mmm and no symmetry. The choice of sample symmetry profoundly affects the selection of harmonic coefficients. For example, in the case of cylindrical sample symmetry (fiber texture) only $k_L^0(y)$ terms are nonzero so the rest are excluded from the summations and the set of C_L^{m0} coefficients is sufficient to describe the effect on the diffraction patterns due to texture. Note that there is no explicit dependence on histogram, thus a single set of harmonic coefficients is used within GSAS to satisfy texture corrections for all powder data sets for a particular crystalline phase.

The crystal harmonic factor, $k_L^m(h)$, is defined for each reflection, h, *via* polar and azimuthal coordinates (φ, β) of a unit vector coincident with h relative to the reciprocal lattice. For most crystal symmetries, φ is the angle between h and the n-th order major rotation axis of the space group (usually the c-axis) and β is the angle between the projections of h and any secondary axis (usually the a-axis) onto the normal plane. In a similar way the sample harmonic factor, $k_L^n(y)$, is defined according to polar and azimuthal coordinates (ψ, γ) of a unit vector coincident with the diffraction vector relative to a coordinate system attached to the external form of the sample. For example, in the case of a rolled steel plate having mmm symmetry, the polar angle, ψ, is frequently measured from the normal direction (ND) and γ is then measured from the rolling direction (RD) in the TD (transverse direction) - RD plane. Thus, the general axis equation becomes

$$O_p(\phi,\beta,\psi,\gamma)=1+\sum_{L=2}^{N_L}\frac{4\pi}{2L+1}\sum_{m=-L}^{L}\sum_{n=-L}^{L}C_L^{mn}k_L^m(\phi,\beta)k_L^n(\psi,\gamma)$$

In a diffraction experiment the crystal reflection coordinates (ϕ, β) are determined by the choice of reflection index (hkl) while the sample coordinates (ψ, γ) are determined by the sample orientation on the diffractometer. In particular, for a neutron TOF experiment each detector bank has a different set of associated sample coordinates (ψ, γ) and a suite of diffraction patterns taken at a variety of sample orientations will survey sample orientation space.

To define the sample coordinates (ψ, γ), we have defined an instrument coordinate system (I, J, K) such that I is normal to the diffraction plane and J is coincident with the direction of the incident radiation beam pointing away from the source. We further define a standard set of right-handed goniometer eulerian angles (Ω, X, Φ) so that Ω and Φ are rotations about I and X is a rotation about J when Ω, X, Φ = 0. Finally, as the sample may be mounted so that the sample coordinate system (I_s, J_s, K_s) does not coincide with the instrument coordinate system (I, J, K), we define three eulerian sample rotation angles (Ω_s, X_s, Φ_s) that describe the rotation from (I, J, K) to (I_s, J_s, K_s). The sample rotation angles are defined so that with the goniometer angles at zero Ω_s and Φ_s are rotations about I and X_s is a rotation about J. The final values of these three sample rotation angles can be refined as part of the Rietveld analysis to accommodate any angular offset in sample mounting. After including the diffraction angle, Θ, the full rotation matrix, M, is

$$M = \mathbf{(\Omega\text{-}\Theta)X(\Phi+\Phi_s)X_s\Omega_s}$$

By transformation of unit Cartesian vectors (100, 010 and 001) with this rotation matrix, the sample orientation coordinates (ψ, γ) are given by

$$cos(\psi) = M\begin{pmatrix}0\\0\\1\end{pmatrix}=$$

$$-sin(\Omega_s)sin(\Omega-\Theta)cos(\Phi+\Phi_s)-sin(\Omega_s)cos(\Omega-\Theta)cos(X)sin(\Phi+\Phi_s)$$
$$-cos(\Omega_s)cos(\Omega-\Theta)sin(X_s)sin(X)-cos(\Omega_s)cos(X_s)sin(\Omega-\Theta)sin(\Phi+\Phi_s)$$
$$+cos(\Omega_s)cos(\Omega-\Theta)cos(X_s)\cos(X)cos(\Phi+\Phi_s)$$

and

$$tan(\gamma) = M\begin{pmatrix}0\\1\\0\end{pmatrix}\Big/M\begin{pmatrix}1\\0\\0\end{pmatrix}=$$

$$[\{cos(\Omega-\Theta)cos(X)cos(\Phi+\Phi_s)-sin(\Omega-\Theta)sin(\Phi+\Phi_s)\}sin(\Omega_s)cos(X_s)-$$
$$\{cos(\Omega-\Theta)cos(X)sin(\Phi+\Phi_s)+sin(\Omega-\Theta)cos(\Phi+\Phi_s)\}cos(\Omega_s)$$

$-sin(\Omega_s)cos(\Omega-\Theta)sin(X)sin(X_s)]$ /
$[\{sin(\Omega-\Theta)sin(\Phi+\Phi_s)-cos(\Omega-\Theta)cos(X)cos(\Phi+\Phi_s)\}sin(X_s)-cos(\Omega-\Theta)sin(X)cos(X_s)]$

The harmonic terms, $k_L^m(\phi,\beta)$ and $k_L^n(\psi,\gamma)$, are developed from

$$k_L^m(\phi,\beta)=\frac{1}{\sqrt{2\pi}}e^{im\beta}\overline{P}_L^m(cos\phi)$$

where the normalized associated Legendre functions, $\overline{P}_L^m(x)$, are defined via a Fourier expansion as

$$\overline{P}_L^m(cos\,\phi)=\sum_{s=0}^{L}a'^{ms}_L\,cos(s\phi)$$

for m even and

$$\overline{P}_L^m(cos\,\phi)=\sum_{s=1}^{L}a'^{ms}_L\,sin(s\phi)$$

for m odd. Each sum is only over either the even or odd values of s, respectively, because of the properties of the Fourier coefficients, a'^{ms}_L. These Fourier coefficients are determined so that the definition

$$\overline{P}_L^m(cos\,\phi)=\overline{P}_L^m(x)=\sqrt{\frac{(L+m)!}{(L-m)!}}\sqrt{\frac{2L+1}{2}}\frac{(-1)^{L-m}}{2^L L!}\left(1-x^2\right)^{-m/2}\frac{d^{L-m}}{dx^{L-m}}\left(1-x^2\right)^L$$

is satisfied. Terms of the form $cos(m\beta)\overline{P}_L^m(cos\,\phi)$ and $sin(m\beta)\overline{P}_L^m(cos\,\phi)$ are combined depending on the symmetry and the value of m along with appropriate normalization coefficients to give the harmonic terms $k_L^m(\phi,\beta)$ and $k_L^n(\psi,\gamma)$. For cubic crystal symmetry, the term $k_L^m(\phi,\beta)$ is obtained directly from the Fourier expansion

$$k_L^m(\phi,\beta)=\sum_{n=0}^{L}B_L^{nm}\overline{P}_L^n(cos\,\phi)cos\,n\beta$$

using the coefficients, B_L^{nm}, as tabulated by Bunge (1982).

The Rietveld refinement of texture then proceeds by constructing derivatives of the profile intensities with respect to the allowed harmonic coefficients, C_L^{mn}, and the three sample orientation angles, Ω_s, X_s, Φ_s, all of which can be adjustable parameters of the refinement. Once the refinement is complete, pole figures for any reflection may be constructed by use of the general axis equation, the refined values for C_L^{mn} and the sample orientation angles Ω_s, X_s, Φ_s. An estimate of the error in these pole figures can be obtained by propagation of error in the general axis equation from the estimated standard deviations associated with the C_L^{mn}.

$$\sigma^2(O_p) = \sum_{L=2}^{N_L}\left(\frac{4\pi}{2L+1}\right)^2 \sum_{m=-L}^{L}\sum_{n=-L}^{L}\sigma^2\left(C_L^{mn}\right)\left(k_L^m\right)^2\left(k_L^n\right)^2$$

The assumption is made that the covariance terms from the least squares refinement for the C_L^{mn} are negligible. This is reasonable considering the orthogonality of the spherical harmonic functions. The magnitude of the texture can be evaluated from the texture index by

$$J = 1 + \sum_{L=2}^{N_L}\frac{1}{2L+1}\sum_{m=-L}^{L}\sum_{n=-L}^{L}|C_L^{mn}|^2$$

If the texture is random then J = 1, otherwise J > 1; for a single crystal J = ∞.

Editing of the spherical harmonic texture correction is done in EDTPRFOH; in GENLES input, output and calculations are done in ODFINP, ODFOUT and ODFCAL. Spherical harmonics calculations are handled by ALMNS, APLMS, FLNH, PLMPSI, QLMN, and QLMNINIT. The graphics program POLFPLOT can be used to generate pole figures, axial distribution plots and Virtual Reality files with 3-dimensional representation of the pole distribution for chosen reflections from the C_l^{mn}. It can also produce ASCII files of calculated pole figures suitable for input to the texture analysis software popLA.

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 that 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 two 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 a monochromator in parallel geometry

$$L = \frac{P_h \cos^2 2\Theta + 1}{\sin^2 \Theta \cos \Theta}$$

where P_h is a refinable polarization fraction defined for each x-ray powder histogram. These functions have slightly different forms but are mathematically identical. A third option is to apply no Lorentz and polarization corrections to the data read into GSAS. This is useful if the powder profile data was corrected for these effects before input to GSAS. Editing of the Lorentz and polarization correction is done in EDTDIFS. In GENLES input and output of the P_h coefficient is in DIFSINP and DIFSOUT; the Lp correction is calculated in DIFSCAL.

Reflection d-spacing and lattice parameters

The d-spacing for a reflection, h=(h,k,l), is given by the standard expression

$$1/d^2 = hgh = Ah^2 + Bk^2 + Cl^2 + 2Dhk + 2Ehl + 2Fkl$$

where g is the reciprocal metric tensor

$$g = \begin{pmatrix} a^{*2} & a^* b^* \cos\gamma^* & a^* c^* \cos\beta^* \\ a^* b^* \cos\gamma^* & b^{*2} & b^* c^* \cos\alpha^* \\ a^* c^* \cos\beta^* & b^* c^* \cos\alpha^* & c^{*2} \end{pmatrix}$$

which is the inverse of the metric tensor

$$G = \begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{pmatrix}$$

The refined coefficients for a powder diffraction pattern are the reciprocal metric tensor elements A-F, as allowed by symmetry. Editing of lattice parameters is done by EDTLAT and input, output and calculations in GENLES are done by CELLINP, CELLOUT, CELLESD and CELLCAL.

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, centidegrees 2Θ or keV. 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_{ph} = DIFC d_p + DIFA d^2_p + 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.

$$\mathrm{DIFC} = 252.816 \cdot 2\,sin\,\Theta\left(L_1 + \sqrt{L_2^2 + L_3^2/16}\right)$$

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/ . 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 Braggís Law.

$\lambda = 2d_p sin\,\Theta$

where λ is the wavelength. In GSAS the powder diffraction profile positions are in centidegrees 2Θ. Thus, the expression for the reflection position is

$$T_{ph} = 200\,sin^{-1}\left(\frac{\lambda_h}{2d_p}\right) + \mathrm{ZERO}$$

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 cannot 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 has modified the $K_{\alpha2}/K_{\alpha1}$ ratio. The same routines in EXPEDT and GENLES that handle the TOF instrument parameters DIFC, DIFA and ZERO also handle LAM1, LAM2 and KRATIO.

Energy dispersive X-ray

The reflection position in an X-ray energy dispersive experiment depends on the selected detector setting angle, Θ, and is given by

$$T_{ph} = 12.398 / (2d_p \sin\Theta) + ZERO$$

This gives the position of the reflection in keV. The relationship between the step or channel number, N, is given by the following simple power series

$$T = \sum_{i=0}^{3} A_i N^i$$

The coefficients for this expression are obtained by fitting peak positions obtained from a standard material at the same time the detector scattering angle is determined.

Profile functions

Each type of powder diffraction data has its own set of profile functions, $H[T-T_{ph}]$. Currently there are a small number installed in GSAS for each type of histogram; they 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 that then calls specific routines for each function. The editing is handled by EDTPRF that calls routines specific to the powder data type.

TOF profile functions

TOF profile function 1

There are currently four 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).

$$H(\Delta T) = N\left[e^{u}\, erfc\, y + e^{v}\, erfc\, z\right]$$

where ΔT is the difference in TOF between the reflection position, T_{ph}, 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 ìHandbook of Mathematical Functions,î 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

$$E(\tau) = 2N e^{\alpha\tau} \text{ for } \tau < 0$$

and

$$E(\tau) = 2N e^{-\beta\tau} \text{ for } \tau > 0$$

for the two exponentials; α and β are the rise and decay coefficients for the exponentials. The Gaussian function is

$$G(\Delta T-\tau)=\frac{1}{\sqrt{2\pi\sigma^2}}exp\left[-(\Delta T-\tau)^2 \big/ 2\sigma^2\right]$$

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

$$u=\frac{\alpha}{2}\left(\alpha\sigma^2+2\Delta T\right)$$

$$v=\frac{\beta}{2}\left(\beta\sigma^2-2\Delta T\right)$$

$$y=\frac{\alpha\sigma^2+\Delta T}{\sqrt{2\sigma^2}}$$

$$z=\frac{\beta\sigma^2-\Delta T}{\sqrt{2\sigma^2}}$$

The three coefficients, α, β and σ^2, each 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.

$$\alpha=\alpha_o+\alpha_1/d$$

$$\beta=\beta_o+\beta_1/d^4$$

$$\sigma^2=\sigma_o^2+\sigma_1^2d^2+\sigma_2^2d^4+\left(\sigma_{1e}^2d^2+\sigma_{2e}^2d^4\right)cos^2\phi$$

Alternatively, a table of the α and β coefficients along with a correction to the reflection position can be used in place of the d-spacing dependences shown above. This facilitates fitting TOF powder diffraction data which does not follow the dependences shown here. Typically data taken on TOF diffractometers that use cryogenic moderators for the neutron source have a more complex behavior for α, β and peak position.

In addition, the ΔT is modified to accommodate the isotropic, ε_i, and anisotropic, ε_a, strain induced displacement of the diffraction lines from their positions expected from the lattice parameters by

$$\Delta T=\left(T-T_{ph}\right)-\varepsilon_i d-\varepsilon_a d\,cos\,\phi-\varepsilon_A\frac{(hk)^2+(hl)^2+(kl)^2}{\left(h^2+k^2+l^2\right)^2}$$

The ε_A is used for the hkl dependence of the strain-induced displacement for cubic materials. 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_{1e}^2, σ_{2e}^2, ε_i, ε_a and ε_A) that are refinable by GENLES. Within GSAS these parameters are named ìalp-0î, ìalp-1î, ìbet-0î, ìbet-1î, ìsig-0î, ìsig-1î, ìsig-2î, ìs1ecî, ìs2ecî, ìrstrî, ìrstaî and ìrscaî, 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.

TOF profile function 2

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:

$$R_k(\tau) = (1-R)\delta(\tau) + R\,e^{-\beta\tau}$$

The two parts describe the leakage of fast and slow neutrons from the moderator and have ëfastí and ëslowí 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

$$P(t) = !\,L(t,\Gamma) + (1 - !)G(t,\Gamma)$$

The Gaussian function is defined above and the Lorentzian function is

$$L(t) = \frac{\Gamma}{2\pi}\frac{1}{\left[\left(\Gamma/2\right)^2 + t^2\right]}$$

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

$$\Gamma_g = \sqrt{(8\,ln\,2)\sigma^2}$$

Thus the two convolutions between the Ikeda-Carpenter function and a Gaussian and Lorentzian are needed. The Gaussian part is

$$G'(\Delta T) = \int G(\Delta T - t)I_k(t)dt$$

or

$$G'(\Delta T) = \frac{\alpha(1-k^2)}{4k^2}\left[\begin{array}{l}\frac{2R\alpha^2\beta k^2}{xyz}h(g,r) + \left\{1 - \frac{R\alpha(1+k)}{z}\right\}h(g,v) + \\ \left\{1 - \frac{R\alpha(1-k)}{x}\right\}h(g,u) - 2\left\{1 - \frac{R\alpha}{y}\right\}h(g,s)\end{array}\right]$$

and

$$h(g,r) = exp(g + r^2)erfc(r)$$

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

$$L'(\Delta T) = \int L(\Delta T - t) I_k(t) dt$$

or

$$L'(\Delta T) = \frac{\alpha(1-k^2)}{2\pi k^2 xyz} \begin{bmatrix} 2R\alpha^2\beta k^2 I(q) + yz\{x - R\alpha(1-k)\} I(p[1-k]) + \\ xy\{z - R\alpha(1+k)\} I(p[1+k]) - 2xz\{y - R\alpha\} I(p) \end{bmatrix}$$

where

$I(q) = Im[e^q \, E_1(q)]$ (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

$$\alpha = \frac{1}{\alpha_o + \alpha_1\lambda}$$

$$\beta = 1/\beta_o$$

$$R = exp\left(-81.799 \big/ \kappa\lambda^2\right)$$

$$\sigma^2 = \sigma_o^2 + \sigma_1^2 d^2 + \sigma_2^2 d^4$$

$$\gamma = \gamma_o + \gamma_1 d + \gamma_2 d^2 + \left(\gamma_{1e} d + \gamma_{2e} d^2\right) cos\,\phi$$

Alternatively, a table of the α, β and κ coefficients along with a correction to the reflection position can be used in place of the d-spacing dependences shown above. This facilitates fitting TOF powder diffraction data which does not follow the dependences shown here. Typically data taken on TOF diffractometers that use cryogenic moderators for the neutron source have a more complex behavior for α, β and peak position.

This function currently has 15 parameters (α_o, α_1, β_o, κ, σ_o^2, σ_1^2, σ_2^2, γ_o, γ_1, γ_2, γ_{1e}, γ_{2e}, DIFC, DIFA and ZERO). 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 6-12î 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 ìalp-0î, ìalp-1î, ìbetaî, ìswitchî, ìsig-0î, ìsig-1î, ìsig-2î, ìgam-0î, ìgam-1î, ìgam-2î, ìsteciî, ìpteciî, ìdifcî, ìdifaî and ìzeroî, respectively.

TOF profile function 3

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.

$$H(\Delta T) = \int E(\Delta T - t)P(t)dt$$

$$H(\Delta T) = (1 - !)N\left[e^{u}\, erfc\, y + e^{v}\, erfc\, z\right] - \frac{2N!}{\pi}\{Im[exp(p\, E_1\, p)] + Im[exp(q\, E_1\, q)]\}$$

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

$$\alpha = \alpha_1 / d$$

$$\beta = \beta_o + \beta_1 / d^4$$

$$\sigma^2 = \sigma_o^2 + \sigma_1^2 d^2 + \sigma_2^2 d^4$$

Alternatively, a table of the α and β coefficients along with a correction to the reflection position can be used in place of the d-spacing dependences shown above. This facilitates fitting TOF powder diffraction data which does not follow the dependences shown here. Typically data taken on TOF diffractometers that use cryogenic moderators for the neutron source have a more complex behavior for α, β and peak position.

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 and includes the origin) have the following expression for the γ coefficient

$$\gamma = \gamma_o + \gamma_1 d + \gamma_2 d^2 + \left(\gamma_{1e} d + \gamma_{2e} d^2\right) cos\, \phi + \gamma_L$$

while the rest have the following expression (note the difference in the last coefficient between these two equations)

$$\gamma = \gamma_o + \gamma_1 d + \gamma_2 d^2 + \left(\gamma_{1e} d + \gamma_{2s} d^2\right) cos\, \phi + \gamma_L$$

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 that will broaden some reflections leaving a sublattice of sharp reflections that correspond to the substructure that 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 ëAí option in EDTPRF. The final term in these two expressions are an empirical extension of the microstrain anisotropy by

$$\gamma_L = \gamma_{11} h^2 + \gamma_{22} k^2 + \gamma_{33} l^2 + 2\gamma_{12} hk + 2\gamma_{13} hl + 2\gamma_{23} kl$$

Thus, this function has 21 coefficients (α_1, β_o, β_1, $\sigma_o{}^2$, $\sigma_1{}^2$, $\sigma_2{}^2$, γ_o, γ_1, γ_2, γ_{1e}, γ_{2e}, γ_{2s}, ε_i, ε_a, ε_A, γ_{11}, γ_{22}, γ_{33}, γ_{12}, γ_{13}, γ_{23}). These are named ìalpî, ìbet-0î, ìbet-1î, ìsig-0î, ìsig-1î, ìsig-2î, ìgam-0î, ìgam-1î, ìgam-2î, ìg1ecî, ìg2ecî, ìgsfî, ìrstrî, ìrstaî, ìrscaî, ìL11î, ìL22î, îL33î, îL12î, îL13î, and îL23î, respectively, within GSAS.

TOF profile function 4

The fourth function uses the same fundamental approach as the first and third functions by employing the result of a convolution between a pair of back-to-back exponentials and a pseudo-Voigt.

$$H(\Delta T) = \int E(\Delta T - t) P(t) dt$$

$$H(\Delta T) = (1 - !)N\left[e^u \, erfc\, y + e^v \, erfc\, z\right] - \frac{2N!}{\pi}\{Im[exp(p\, E_1\, p)] + Im[exp(q\, E_1\, q)]\}$$

The definitions of the various components are similar to those given above with

$$\Delta T = (T - T_{ph}) - \varepsilon_i d - \varepsilon_a d \cos\phi - \varepsilon_A \frac{(hk)^2 + (hl)^2 + (kl)^2}{(h^2 + k^2 + l^2)^2}$$

$$\alpha = \alpha_1 / d$$

$$\beta = \beta_o + \beta_1 / d^4$$

for the exponential terms and

$$\sigma^2 = \sigma_1^2 d^2 + \sigma_2^2 d^4 + \sigma_S^2 d^6$$

for the Gaussian contribution. The Lorentzian contribution has two forms,

$$\gamma = \gamma_2 d^2 + \gamma_{2e} d^2 \cos\phi + \gamma_S d^3$$

or

$$\gamma = \gamma_2 d^2 + \gamma_{2s} d^2 \cos\phi + \gamma_S d^3$$

for modeling particle size broadening arising from stacking faults.

Alternatively, a table of the α and β coefficients along with a correction to the reflection position can be used in place of the d-spacing dependences shown above. This facilitates fitting TOF powder diffraction data which does not follow the dependences shown here. Typically data taken on TOF diffractometers that use cryogenic moderators for the neutron source have a more complex behavior for α, β and peak position.

The Gaussian and Lorentzian portions ascribed to microstrain broadening, σ_S^2 and γ_S, are now described by a semi-empirical form that was developed by P. Stephens, J. Appl. Cryst., 32, 281-289 (1999). Beginning with the expression for a reflection d-spacing

$$\frac{1}{d_{hkl}^2} = M_{hkl} = \alpha_1 h^2 + \alpha_2 k^2 + \alpha_3 l^2 + \alpha_4 kl + \alpha_5 hl + \alpha_6 hk$$

we develop for the triclinic case a variance-covariance matrix which accommodates the possible variation in each of the components of this expression giving the microstrain broadening, $\Gamma_S^2 = \sigma^2(M_{hkl})$, or

$$\Gamma_S^2 = \sum_{i,j} S_{ij} \frac{\partial M}{\partial \alpha_i} \frac{\partial M}{\partial \alpha_j}$$

Given the individual partial derivatives

$$\frac{\partial M}{\partial \alpha_1} = h^2\ , \frac{\partial M}{\partial \alpha_2} = k^2\ , \frac{\partial M}{\partial \alpha_3} = l^2\ , \frac{\partial M}{\partial \alpha_4} = kl\ , \frac{\partial M}{\partial \alpha_5} = hl \text{ and } \frac{\partial M}{\partial \alpha_6} = hk$$

the variance-covariance matrix becomes

$$\frac{\partial M}{\partial \alpha_i} \frac{\partial M}{\partial \alpha_j} = \begin{bmatrix} h^4 & h^2k^2 & h^2l^2 & h^2kl & h^3l & h^3k \\ h^2k^2 & k^4 & k^2l^2 & k^3l & hk^2l & hk^3 \\ h^2l^2 & k^2l^2 & l^4 & kl^3 & hl^3 & hkl^2 \\ h^2kl & k^3l & kl^3 & k^2l^2 & hkl^2 & hk^2l \\ h^3l & hk^2l & hl^3 & hkl^2 & h^2l^2 & h^2kl \\ h^3k & hk^3 & hkl^2 & hk^2l & h^2kl & h^2k^2 \end{bmatrix}$$

Then the expression for the microstrain becomes

$$\Gamma_S^2 = \sum_{HKL} S_{HKL} h^H k^K l^L\ , H + K + L = 4$$

By collecting terms this expression for the triclinic case becomes

$$\begin{aligned} \Gamma_S^2 = {} & S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3\left(S_{220}h^2k^2 + S_{202}h^2l^2 + S_{022}k^2l^2\right) + \\ & 2\left(S_{310}h^3k + S_{103}hl^3 + S_{031}k^3l + S_{130}hk^3 + S_{301}h^3l + S_{013}kl^3\right) + \\ & 4\left(S_{211}h^2kl + S_{121}hk^2l + S_{112}hkl^2\right) \end{aligned}$$

Thus there are 15 possible coefficients S_{400}, S_{040}, S_{004}, S_{220}, S_{202}, S_{002}, S_{310}, S_{130}, S_{301}, S_{103}, S_{031}, S_{013}, S_{211}, S_{121} and S_{112}. The two contributors to the Gaussian and Lorentzian broadening, σ_S^2 and γ_S, are found from the action of a mixing coefficient, η, on Γ_S^2 by

$\gamma_S = !\,\Gamma_S$ and $\sigma_S = (1 - !\,)\Gamma_S$.

For Laue symmetries other than $\bar{1}$ (triclinic), the symmetry imposes restrictions on the allowed S_{HKL} terms. Consequently for the other cases the expression for Γ_S^2 become

Monoclinic (2/m ñ b axis unique; others similar)

$$\Gamma_S^2 = S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3S_{202}h^2l^2 + 3\left(S_{220}h^2k^2 + S_{022}k^2l^2\right) + 2\left(S_{301}h^3l + S_{103}hk^3\right) + 4S_{121}hk^2l$$

Orthorhombic (mmm)

$$\Gamma_S^2 = S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3\left(S_{220}h^2k^2 + S_{202}h^2l^2 + S_{022}k^2l^2\right)$$

Tetragonal (4/mmm and 4/m)

$$\Gamma_S^2 = S_{400}\left(h^4 + k^4\right) + S_{004}l^4 + 3S_{220}h^2k^2 + 3S_{202}\left(h^2l^2 + k^2l^2\right)$$

Trigonal ($\overline{3}$)

$$\Gamma_S^2 = S_{400}\left(h^4 + k^4 + 2h^3k + 2hk^3 + 3h^2k^2\right) + S_{004}l^4 + 3S_{202}\left(h^2l^2 + k^2l^2 + hkl^2\right) + S_{301}\left(2h^3l - 2k^3l - 6hk^2l\right) + 4S_{211}\left(h^2kl + hk^2l\right)$$

Trigonal ($\overline{3}$ - rhombohedral setting)

$$\Gamma_S^2 = S_{400}\left(h^4 + k^4 + l^4\right) + 3S_{220}\left(h^2k^2 + h^2l^2 + k^2l^2\right) + 2S_{310}\left(h^3k + k^3l + hl^3\right) + 2S_{130}\left(h^3l + kl^3 + hk^3\right) + 4S_{211}\left(h^2kl + hk^2l + hkl^2\right)$$

Trigonal ($\overline{3}m1$)

$$\Gamma_S^2 = S_{400}\left(h^4 + k^4 + 3h^2k^2 + 2h^3k + 2hk^3\right) + S_{004}l^4 + 3S_{202}\left(h^2l^2 + k^2l^2 + hkl^2\right) + S_{301}\left(3h^2k - 3hk^2 + 2h^3 - 2k^3\right)l$$

Trigonal ($\overline{3}m1$ - rhombohedral setting)

$$\Gamma_S^2 = S_{400}\left(h^4 + k^4 + l^4\right) + 3S_{220}\left(h^2k^2 + h^2l^2 + k^2l^2\right) + 2S_{310}\left(h^3k + hl^3 + k^3l + hk^3 + h^3l + kl^3\right) + 4S_{211}\left(h^2kl + hk^2l + hkl^2\right)$$

Trigonal ($\overline{3}1m$)

$$\Gamma_S^2 = S_{400}\left(h^4 + k^4 + 3h^2k^2 + 2h^3k + 2hk^3\right) + S_{004}l^4 + 3S_{202}\left(h^2l^2 + k^2l^2 + hkl^2\right) + 4S_{211}\left(h^2kl + hk^2l\right)$$

Hexagonal (6/m and 6/mmm)

$$\Gamma_S^2 = S_{400}\left(h^4 + k^4 + 3h^2k^2 + 2h^3k + 2hk^3\right) + S_{004}l^4 + 3S_{202}\left(h^2l^2 + k^2l^2 + hkl^2\right)$$

Cubic (m3 and m3m)

$$\Gamma_S^2 = S_{400}\left(h^4 + k^4 + l^4\right) + 3S_{220}\left(h^2k^2 + h^2l^2 + k^2l^2\right)$$

Thus, this function has between 14 and 27 coefficients (α_1, β_o, β_1, σ_1^2, σ_2^2, γ_2, γ_{2e}, γ_{2s}, ε_i, ε_a, ε_A, η, and the S_{HKL} as required by symmetry). These are named ìalpî, ìbet-0î, ìbet-1î, ìsig-1î, ìsig-2î, ìgam-2î, ìg2ecî,îgsfî, ìrstrî, ìrstaî, ìrscaî, ìetaî, ìS400î, etc., respectively, within GSAS.

The editing of the coefficients for all four functions is done by EDTPTP1. Calculations are handled through PRFCCAL that calls EXPGAUS, IKCARVT, EXPSTVGT, and EXPSTVTS for the four 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 that 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

$$\sigma^2 = \sigma_o^2 + \sigma_1^2 d^2 + \sigma_2^2 d^4 + \left(\sigma_{1e}^2 d^2 + \sigma_{2e}^2 d^4\right) cos^2 \phi$$

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 that is frequently expressed as percent strain or fractional strain as a full width at half maximum.

$$S = \frac{1}{C}\sqrt{(8\,ln\,2)\left(\sigma_1^2 - \sigma_{1i}^2\right)}\,100\%$$

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

$$S_{||} = \frac{1}{C}\sqrt{(8\,ln\,2)\left(\sigma_1^2 + \sigma_{1e}^2 - \sigma_{1i}^2\right)}\,100\%$$

The perpendicular component is then

$$S_{\perp} = \frac{1}{C}\sqrt{(8\,ln\,2)\left(\sigma_1^2 - \sigma_{1i}^2\right)}\,100\%$$

For the second and third functions, the sample broadening is assumed to be Lorentzian and examination of the expression

$$\gamma = \gamma_o + \gamma_1 d + \gamma_2 d^2 + \left(\gamma_{1e} d + \gamma_{2e} d^2\right) cos\,\phi$$

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

$$S_{||} = \frac{1}{C}\left(\gamma_1 + \gamma_{1e}\right)100\%$$

$$S_{\perp} = \frac{1}{C}\gamma_1\ 100\%$$

For the fourth function the microstrain is best described by a surface in reciprocal space in which the radial distance from the origin is given by

$$S_S(hkl) = \frac{d^2}{C}\sqrt{\sum_{HKL} S_{HKL} h^H k^K l^L}\ 100\%$$

where the function is the appropriate one for the Laue symmetry.

Particle size broadening

In reciprocal space isotropic particle size broadening makes all points the same size independent of the distance from the origin. Thus,

$\Delta d^* =$ constant

The reciprocal of this quantity is then the average particle size. In real space (for TOF) the broadening is

$\Delta d/d^2 =$ 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 $\mu sec^2/\ ^2$ and is a variance, the particle size (p) then is given by

$$p = \frac{CK}{\sqrt{(8\,ln\,2)\sigma_2^2}}$$

where C is the diffractometer constant (DIFC), K is the Scherrer constant and the units for p are . The anisotropy in the particle size can also be determined relative to the broadening axis so that the parallel component is

$$p_{||} = \frac{CK}{\sqrt{(8\,ln\,2)\left(\sigma_2^2 + \sigma_{2e}^2\right)}}$$

and the perpendicular component is

$$p_\perp = \frac{CK}{\sqrt{(8\,ln\,2)\sigma_2^2}}$$

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

$$p_{||} = \frac{CK}{\gamma_2 + \gamma_{2e}}$$

$$p_\perp = \frac{CK}{\gamma_2}$$

In the presence of stacking faults, the γ_{2s} coefficient can be used to obtain the average distance between faults, p_s, 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 or fourth function would best fit diffraction data taken on high resolution TOF diffractometers with tall detectors.

CW profile functions

CW profile function 1

There are currently four 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).

$$H(\Delta T) = N\left(1 - \frac{\Delta T'|\Delta T|A_s}{tan\,\Theta}\right)exp\left(\frac{-\Delta T'^2}{2\sigma^2}\right)$$

the normalization factor, N, is

$$N = \frac{1}{\sqrt{2\pi\sigma^2}}$$

and the modified 2Θ difference is

$$\Delta T' = \Delta T + \frac{F_1}{tan\,2\Theta}$$

The variance of the peak, σ^2, varies with 2Θ as

$$\sigma^2 = U\,tan^2\,\Theta + V\,tan\,\Theta + W + {F_2}\big/{tan^4\,\Theta}$$

Thus there are six profile coefficients U, V, W, A_S, F_1 & F_2 for constant wavelength neutron data; these are named ìUî, ìVî, ìWî, ìasymî, ìF1î, and ìF2î, respectively in GSAS. This function and its derivatives are calculated in MODGAUS, the coefficients are edited by EDTPTP2.

CW profile function 2

The second and considerably more successful function employs a multi-term Simpsonís 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

$$F(\Delta T') = !\,L(\Delta T',\Gamma) + (1-!)G(\Delta T',\Gamma)$$

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

$$\Gamma_g = \sqrt{(8\,ln\,2)\sigma^2}$$

The 2Θ difference modified for asymmetry, A_S, and sample shift, S_S, is

$$\Delta T' = \Delta T + \frac{f_i A_s}{tan\,2\Theta} + S_s\,cos\,\Theta + T_s\,sin\,2\Theta$$

where the number of terms in the sum depends on the size of A_s. The corresponding Simpsonís rule coefficients, g_i and f_i, depend on the number of terms in the summation. In the case of Bragg-Brentano 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

$$\mu_{eff} = \frac{-9000}{\pi R T_s}$$

The variance of the peak, σ_2, varies with 2Θ as

$$\sigma^2 = U\,tan^2\,\Theta + V\,tan\,\Theta + W + P\!\Big/\!cos^2\,\Theta$$

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

$$\gamma = \frac{X + X_e\,cos\,\phi}{cos\,\Theta} + \left(Y + Y_e\,cos\,\phi\right)tan\,\Theta$$

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 ìstacking fault vectorsî, 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)

$$\gamma = \frac{X + X_s\,cos\,\phi}{cos\,\Theta} + \left(Y + Y_e\,cos\,\phi\right)tan\,\Theta$$

This function gives the different anisotropic Scherrer broadening that is associated with the presence of stacking faults and is similar to that used in TOF functions 2,3 and 4 shown above.

Thus there are twelve coefficients for this function (U, V, W, X, Y, T_s, A_s, P, S_s, Y_e, X_e and X_s). Within GSAS these are named ìGUî, ìGVî, ìGWî, ìLXî, ìLYî, ìtrnsî, ìasymî, ìshftî, ìGPî, ìsteci, ìptecî and ìsfecî, respectively. This function gives a better fit to asymmetric profiles than the first one and shows less correlation with the lattice parameters. It does not do well treating the reflection asymmetry due to axial divergence at low angles (2Θ<10). The function and its derivatives are generated by PSCVGT.

CW profile function 3

The third CW profile function is a similar variation on the pseudo-Voigt function used in the second function. However, it uses a much more successful description of the reflection asymmetry due to axial divergence described by Finger, Cox & Jephcoat, J. Appl. Cryst., 27,892-900 (1994) as an implementation of the peak shape function described by Van Laar & Yelon, J. Appl. Cryst., 17, 47-54 (1984).

This function is formed by a convolution of a pseudo-Voigt with the result of considering the intersection of the Debye Scherrer diffraction cone that is at the scattering angle of 2Θ and a finite height slit positioned below 2Θ by τ. The slit intercept function is

$$D(\tau)=\frac{L^2 \sin 2\Theta}{4HSh(\tau)\cos(2\Theta-\tau)}W(\tau)$$

where L is the diffractometer radius, H and S are the sample and detector heights. The functions $h(\tau)$ and $W(\tau)$ are

$$h(\tau)=L\sqrt{\cos^2(2\Theta-\tau)/\cos^2 2\Theta-1}$$

$$W(\tau)=H+S-h(\tau) \text{ for } \tau_{infl}\le\tau\le\tau_{min}$$

$$W(\tau)=2\min(H,S) \text{ for } 0\le\tau\le\tau_{infl}$$

and $W(\tau)=0$ elsewhere. The inflection point is where the entire slit sees the sample and is found by

$$\tau_{infl}=2\Theta-\cos^{-1}\left[\cos 2\Theta\sqrt{\left(\frac{H-S}{L}\right)^2+1}\right]$$

and the point of first contact between the slit and cone is

$$\tau_{min}=2\Theta-\cos^{-1}\left[\cos 2\Theta\sqrt{\left(\frac{H+S}{L}\right)^2+1}\right]$$

The convolution between this function and the pseudo-Voigt, $P(\Delta T)$, is

$$H(\Delta T)=\int P(\Delta T-\tau)D(\tau)d\tau=\frac{L^2\sin 2\Theta}{4HS}\int\frac{W(\tau)P(\Delta T-\tau)}{h(\tau)\cos(2\Theta-\tau)}d\tau$$

The range of integration is $0\le\tau\le\tau_{min}$. This integral cannot be performed analytically for the pseudo-Voigt function so a Gauss-Legendre quadrature is used instead

$$H(\Delta T)=\frac{L^2\sin 2\Theta}{4HS}\frac{\sum_{i=M}^{N} w_i\left[\frac{W(\delta_i)P(\Delta T-\delta_i)}{h(\delta_i)\cos\delta_i}\right]}{\sum_{i=M}^{N} w_i\left[\frac{W(\delta_i)}{h(\delta_i)\cos\delta_i}\right]}$$

where δ_i and w_i are the displacements and weights for the points used in the summations. The range of the sum is from M=N/2+1 to N where N is chosen to give the number of intervals needed to produce a sufficiently accurate integration. The range of N used here is 10-100 depending on how large τ_{min} is.

This function is described only by the two ratios, H/L and S/L, which can be specified exactly from the diffractometer geometry. This CW profile function in GSAS contains these two parameters, ìH/Lî and ìS/Lî, which can be refined when diffraction data of sufficiently low 2Θ are present.

The functional form of the pseudo-Voigt used in this function is exactly the same as used in the second CW function. The Gaussian 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. 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 and includes the origin) have the following expression for the γ coefficient

$$\gamma = \frac{X + X_e\,cos\phi}{cos\Theta} + \left(Y + Y_e\,cos\phi + \gamma_L d^2\right)tan\Theta$$

while the rest have the following expression (note the difference in one of the coefficients between these two equations)

$$\gamma = \frac{X + X_s\,cos\phi}{cos\Theta} + \left(Y + Y_e\,cos\phi + \gamma_L d^2\right)tan\Theta$$

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 that will broaden some reflections leaving a sublattice of sharp reflections that correspond to the substructure that 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 ëA' option in EDTPRF. The γ_L term in these two expressions are an empirical extension of the microstrain anisotropy by

$$\gamma_L = \gamma_{11}h^2 + \gamma_{22}k^2 + \gamma_{33}l^2 + 2\gamma_{12}hk + 2\gamma_{13}hl + 2\gamma_{23}kl$$

Thus there are nineteen coefficients for this function (U, V, W, P, X, Y, S/L, H/L, T_s, S_s, Y_e, X_e, X_s, γ_{11}, γ_{22}, γ_{33}, γ_{12}, γ_{13}, γ_{23}). Within GSAS these are named ìGUî, ìGVî, ìGWî, ìGPî, ìLXî, ìLYî, ìS/Lî, ìH/Lî, ìtrnsî, ìshftî, ìstecî, ìptecî, ìsfecî, ìL11î, ìL22, îL33î, îL12î, îL13î and îL23î, respectively. This function gives a far better fit to asymmetric profiles than either of the first two functions and provides an excellent fit to even very low angle (2Θ~1) synchrotron data. The function and its derivatives are generated by PSVGTFCJ and PSVFCJ.

CW profile function 4

The fourth CW profile uses the same convolution of a pseudo-Voigt and asymmetry function used for the third function. This function also uses the microstrain broadening description of P. Stephens, J. Appl. Cryst., 32, 281-289 (1999).

The Gaussian variance of the peak, σ_2, varies with 2Θ as

$$\sigma^2 = \left(U + \sigma_S^2 d^4\right)tan^2\Theta + V\,tan\Theta + W + P/cos^2\Theta$$

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. 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 and includes the origin) have the following expression for the γ coefficient

$$\gamma = \frac{X + X_e \, cos\,\phi}{cos\,\Theta} + \left(Y + Y_e \, cos\,\phi + \gamma_S d^2\right) tan\,\Theta$$

while the rest have the following expression (note the difference in one of the coefficients between these two equations)

$$\gamma = \frac{X + X_s \, cos\,\phi}{cos\,\Theta} + \left(Y + Y_e \, cos\,\phi + \gamma_S d^2\right) tan\,\Theta$$

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 that will broaden some reflections leaving a sublattice of sharp reflections that correspond to the substructure that 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 ëA' option in EDTPRF.

The Gaussian and Lorentzian portions ascribed to microstrain broadening, σ_S^2 and γ_S, are described by a semi-empirical form that was developed by P. Stephens, J. Appl. Cryst., 32, 281-289 (1999). As used in the fourth TOF profile function, the expression for the microstrain is

$$\Gamma_S^2 = \sum_{HKL} S_{HKL} h^H k^K l^L \text{ , } H + K + L = 4$$

which for the triclinic case is

$$\begin{aligned}\Gamma_S^2 = {} & S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3\left(S_{220}h^2k^2 + S_{202}h^2l^2 + S_{022}k^2l^2\right) + \\ & 2\left(S_{310}h^3k + S_{103}hl^3 + S_{031}k^3l + S_{130}hk^3 + S_{301}h^3l + S_{013}kl^3\right) + \\ & 4\left(S_{211}h^2kl + S_{121}hk^2l + S_{112}hkl^2\right)\end{aligned}$$

The two contributors to the Gaussian and Lorentzian broadening, σ_S^2 and γ_S, are found from the action of a mixing coefficient, η, on Γ_S^2 by

$\gamma_S = !\,\Gamma_S$ and $\sigma_S = (1 - !\,)\Gamma_S$.

For Laue symmetries other than $\overline{1}$ (triclinic), the symmetry imposes restrictions on the allowed S_{HKL} terms. For the other cases the expression for Γ_S^2 can be found in the description for the fourth TOF profile function above.

Thus, there are between 14 and 27 coefficients for this function (U, V, W, P, X, X_e, T_s, S_s, X_s, S/L, H/L, η, and the S_{HKL} as required by symmetry). Within GSAS these are named ìGUî, ìGVî, ìGWî, ìGPî, ìLXî, ìptecî, ìtrnsî, ìshftî, ìsfecî, ìS/Lî, ìH/Lî, ìetaî, ìS400î, etc., respectively. This function gives a far better fit to asymmetric profiles than either of the first two functions and provides an excellent fit to even very low angle (2Θ~1) synchrotron data. It also gives an excellent fit to the irregular broadening caused by the most general form of microstrain broadening. The function and its derivatives are generated by PSVFCJS and PSVFCJ.

The editing of the coefficients for these functions for neutron data is done in EDTPTP2. The coefficients for x-ray data are edited by EDTPTP3. The pairs of peaks arising from the α_1-α_2 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

$$\Delta 2\Theta = \left(\Delta d/d\right) tan\,\Theta$$

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

$$\gamma = \frac{X + X_s\, cos\,\phi}{cos\,\Theta} + \left(Y + Y_e\, cos\,\phi\right) tan\,\Theta$$

and the strain term is the one that varies with *tan* Θ. 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

$$S = \frac{\pi}{18000}\left(Y - Y_i\right)100\%$$

As in the case of TOF data the parallel and perpendicular anisotropic strain components can be calculated by

$$S_{||} = \frac{\pi}{18000}\left(Y + Y_e - Y_i\right)100\%$$

$$S_{\perp} = \frac{\pi}{18000}\left(Y - Y_i\right)100\%$$

For the fourth function the microstrain is best described by a surface in reciprocal space in which the radial distance from the origin is given by

$$S_S(hkl) = \frac{\pi d^2}{18000}\sqrt{\sum_{HKL} S_{HKL} h^H k^K l^L}\ 100\%$$

where the function is the appropriate one for the Laue symmetry.

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 Braggís 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

$$p = \frac{18000 K\lambda}{\pi X}$$

where K is the Scherrer constant. The units are . The anisotropic particle size components are given by

$$p_{||} = \frac{18000 K\lambda}{\pi(X + X_e)}$$

$$p_{\perp} = \frac{18000 K\lambda}{\pi X}$$

In a similar way to the TOF functions #2, #3 and #4, 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

$$p = \frac{18000K\lambda}{\pi\sqrt{(8\,ln\,2)P}}$$

and again the units are .

Energy dispersive profile function

The profiles thus far obtained from X-ray energy dispersive experiments are dominated by electronic broadening in the detector system. This broadening is Gaussian and is given by

$$H(\Delta T') = \frac{1}{\sqrt{2\pi\sigma^2}} exp\left[-\Delta T'^2 \big/ 2\sigma^2\right]$$

The Gaussian broadening is expressed by a simple power series in energy

$\sigma^2 = AT^2 + BT + C$ where T is the X-ray energy in keV.

Since X-ray energy dispersive experiments are frequently performed at high pressure, frequently the diffraction pattern is affected by deviatoric stress. Thus, the reflection positions are given by

$$\Delta T = (T - T_{ph}) - \left[\varepsilon_a d\, cos\,\phi + \varepsilon_A \frac{(hk)^2 + (hl)^2 + (kl)^2}{(h^2 + k^2 + l^2)^2}\right]T$$

Thus, there are five coefficients for this profile function ìAî, ìBî, ìCî, ìε_aî and ìε_Aî. Within GSAS these are named ìAî, ìBî, îCî, ìdsî, and ìcdsî, respectively. These coefficients are edited in routine EDTPTP4 in EXPEDT, and GENLES uses EDSGAUS and EDSGAUS1 to calculate this function and its derivatives.

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.

Minimization function

The minimization function in GENLES can be made up of several components.

$$M = \sum M_h$$

Each component M_h can be made up of single crystal diffraction data (M_s), powder diffraction data (M_p) or stereochemical restraint data (M_r). These components each occupy separate histograms within the GSAS data structure. In turn these components are discussed next along with any applicable statistical measures (R-values, etc.) for the quality of the minimization.

Single crystal diffraction data

For single crystal data the contribution to the minimization function in GSAS is usually

$$M_s = \sum w\left(F_o^2 - SF_c^2\right)^2$$

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

$$R = \frac{\sum\left|F_o^2 - SF_c^2\right|}{\sum\left|F_o^2\right|}$$

and

$$R_w = \sqrt{\frac{M_s}{\sum w\left|F_o^2\right|}}$$

The reduced χ^2 or "goodness of fitî is defined by the minimization function as

$$\chi^2 = \frac{M_s}{\left(N_{obs} - N_{var}\right)}$$

An alternative minimization function for single crystal data is

$$M_s = \sum w\left(|F_o| - |SF_c|\right)^2$$

In this case the residuals become

$$R = \frac{\sum\left||F_o| - |SF_c|\right|}{\sum|F_o|}$$

and

$$R_w = \sqrt{\frac{M_s}{\sum w|F_o|}}$$

The χ^2 is defined as above.

Powder diffraction data

In analogy to the single crystal case, the contribution to the minimization function for powder diffraction data is the function (Rietveld, J. Appl. Cryst. 2, 65-71, 1969)

$$M_p = \sum w(I_o - I_c)^2$$

Each powder diffraction pattern used in the refinement occupies a separate histogram within GSAS and forms a separate contribution to the minimization function. The quality of least squares refinement in this case is also indicated by some residual functions; there is a set for each powder histogram. These cover the entire pattern except excluded regions (marked ìAllî). A second set is also shown (marked ì-Bkndî) that are calculated for only the Bragg contribution to the diffraction pattern. In analogy to the single crystal case, the residuals are defined as:

$$R_p = \sum|I_o - I_c| \Big/ \sum I_o$$

and

$$R_{wp} = \sqrt{M_p \Big/ \sum wI_o^2}$$

for the ìAllî case. The ì-Bkndî residuals are computed from

$$R_{pb} = \sum \frac{|I_o - I_c| \cdot |I_o - I_b|}{I_o} \Bigg/ \sum|I_o - I_b|$$

and

$$R_{wpb} = \sqrt{\sum w\left((I_o - I_c)(I_o - I_b) \big/ I_o\right)^2 \Bigg/ \sum w(I_o - I_b)^2}$$

where I_b is the background contribution to the profile.

The reduced χ^2 is also defined the same way as in the single crystal case by

$$\chi^2 = \frac{M_p}{N_{obs} - N_{var}}$$

One can hand calculate an ìexpected R_{wp}î 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 ìtrueî 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.

Soft restraints data

In GSAS it is also possible to provide as a set of observations the expected values for a set of stereochemical restraints (Von Dreele, J. Appl. Cryst., 34, 1084-1089, 1999) assigning to each an appropriate standard deviation. These so-called ìsoft restraintsî are then used to generate a minimization function

$$\begin{aligned} M_r = {} & f_a \sum_{i=1}^{N_a} w_i(\alpha_{oi} - \alpha_{ci})^2 + f_c \sum_{i=1}^{N_c} w_i(c_{oi} - c_{ci})^2 + f_d \sum_{i=1}^{N_d} w_i(d_{oi} - d_{ci})^2 \\ & + f_t \sum_{i=1}^{N_t} w_i(t_{oi} - t_{ci})^2 + f_p \sum_{i=1}^{N_p} w_i(-p_{ci})^2 + f_v \sum_{i=1}^{N_v} w_i(v_{oi} - v_{ci})^4 \\ & + f_h \sum_{i=1}^{N_h} w_i(h_{oi} - h_{ci})^2 + f_x \sum_{i=1}^{N_x} w_i(x_{oi} - x_{ci})^2 + f_R \sum_{i=1}^{N_R} w_i(-R_{ci})^2 \\ & + f_z \sum_{i=1}^{N_z} w_i(-z_i)^2 \end{aligned}$$

These terms are stereochemical minimization functions for bond angles, unit cell contents, bond distances, torsion angles, planar groups, van der Waals repulsions, hydrogen bonds, chiral volumes, coupled torsion angle pseudopotentials and positive pole figures, respectively. Each one occupies a separate histogram in GSAS. Each restraint term has a weight, $w_i=1/\sigma_i^2$; the individual σ_i values are estimated from, for example, the distribution of bond lengths in other small molecules. The weight factors (f_a, f_d, etc.) are normally set to unity during refinement, however their values can be adjusted to increase or reduce the effect of each restraint component on the minimization function. Usually f 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 some stereochemical restraint. The large contribution in the beginning of the analysis is used to avoid diverging refinements. Each of these restraint terms will be discussed in turn.

Bond angle restraints

The bond angles for the atom sequence A-B-C are calculated in the usual way by

$$\alpha_c = cos^{-1}\left(\frac{v_{BA} \cdot v_{BC}}{|v_{BA}||v_{BC}|}\right)$$

Derivatives of these angles are computed numerically by individually displacing each atom by 0.005 along each Cartesian axis in turn and recomputing the angle. The derivatives are then transformed to crystal coordinates before using to build the least squares matrix. These calculations are done in ANGCALC and BNDAGL. The angle restraints are edited in subroutine EDTANG.

Unit cell contents restraints

The unit cell contents restraint is a simple sum of the site fractions for selected atoms over the entire unit cell. Each term in the sum is multiplied by a user selected scaling factor.

$$c_c = \sum_{i=1}^{N} m_i f_i s_i$$

where m_i is the number of times the particular site occurs in the unit cell, f_i is the atom site fraction and s_i is the user chosen multiplier. The sum is over the atom site chosen by the user to be included. The user chosen multiplier is keyed to the atom type. Depending on the choice of this multiplier many different unit cell sums can be restrained. For example, if all s_i=1.0 then just the unit cell contents for a particular atom type can be restrained. If s_i is chosen as the atom valence and all atom sites are included in the sum then a restraint for charge neutrality over the entire unit cell can be made. These calculations are done in CHEMCMP. The unit cell contents restraints are edited in subroutine EDTCMP.

Bond distance restraints

The bond distances for the atom sequence A-B are calculated in the usual way by

$$d_c = |v_{AB}|$$

Derivatives of these distances are determined analytically. These calculations are done in BNDCALC. The bond distance restraints are edited in subroutine EDTBND.

Torsion angle restraints

The torsion angle for the atom sequence A-B-C-D is calculated from the vectors v_{AB}, v_{BC} and v_{CD}. The vectors are normalized and the torsion angle is calculated from the results of three dot products

$$P_1 = \frac{v_{AB} \cdot v_{BC}}{|v_{AB}||v_{BC}|} \qquad P_2 = \frac{v_{AB} \cdot v_{CD}}{|v_{AB}||v_{CD}|} \qquad P_3 = \frac{v_{BC} \cdot v_{CD}}{|v_{BC}||v_{CD}|}$$

$$t_c = cos^{-1}\left(\frac{P_1P_3 - P_2}{\sqrt{1-P_1^2}\sqrt{1-P_3^2}}\right)$$

and if

$$\begin{vmatrix} v_{AB} \\ v_{BC} \\ v_{CD} \end{vmatrix} \le 0$$

then $t_c = -t_c$

This gives a torsion angle that is zero when the AB and CD bonds are eclipsed and 180 when staggered. Derivatives of these torsion angles are computed numerically by individually displacing each atom by 0.005 along each Cartesian axis and recomputing the angle in turn. The derivatives are then transformed to crystal coordinates before using to build the least squares matrix. These calculations are done in FLTCALC and TORSHN. The angle restraints are edited in subroutine EDTTOR.

Planar group restraints

The planar group restraint is computed by determining the best plane through a group of atoms and determining the distance of each atom from this best plane. The best plane is found by first transforming the coordinates, x_i, of the set of N atoms to a Cartesian set, X_i, with the origin at the centroid of the group by the following

$$X_i = L\left(x_i - \frac{1}{N}\sum_{i=1}^{N} x_i\right) \text{where } L = \begin{pmatrix} a & b\,cos\,\gamma & c\,cos\,\beta \\ 0 & b\,sin\,\alpha^* sin\,\gamma & 0 \\ 0 & -b\,cos\,\alpha^* sin\,\gamma & c\,sin\,\beta \end{pmatrix}$$

The restraints are to minimize the individual atom displacements from the best plane. These calculations are done in BMPCALC and BSTPLN. The hydrogen bond restraints are edited in subroutine EDTPLN.

van der Waals repulsion restraints

The van der Waals distances for the atom sequence A-B are calculated for only macromolecular phases in the usual way by

$b_c = |v_{AB}|$

Candidate distances are obtained by considering all possible ëBí atoms within a 3x3x3 unit cell block around the ëAí atom. Those that are closer than the sum of predetermined atom van der Waals radii are included in a restraint to that distance. Atoms farther away are not considered; thus this restraint is only a repulsive one. Atoms within adjacent amino acid residues are rejected from consideration as are atoms with site fractions less than unity. Thus this restraint does include both intermolecular and intramolecular contacts. Derivatives of these distances are determined analytically. These calculations are done in BMPCALC. Use is made of a fast search algorithm in which all the atoms within the macromolecule and its immediate neighborhood are first binned into 6x6x6 boxes. The search for nonbonded contacts is then done only on a 3x3x3 block of these boxes for each atom. The van der Waals restraints are edited in subroutine EDTBMP.

Hydrogen bond restraints

The hydrogen bond distances for the atom sequence A-B are calculated for only macromolecular phases in the usual way by

$$h_c = |v_{AB}|$$

Candidate distances are obtained by considering all possible acceptor/donor ëBí atoms within a 3x3x3 unit cell block around each donor/acceptor ëAí atom. Those that are closer than the sum of predetermined atom hydrogen bond radii plus a tolerance are included in a restraint to that distance. Atoms farther away are not considered. Atoms within adjacent amino acid residues are rejected from consideration as are atoms with site fractions less than unity. Thus this restraint does include both intermolecular and intramolecular contacts. Derivatives of these distances are determined analytically. These calculations are done in BMPCALC. The hydrogen bond restraints are edited in subroutine EDTBMP.

Chiral volume restraints

The chiral volume for a A-BCD(H) group is computed for the v_{AB}, v_{AC} and v_{AD} vector triplet by the determinant

$$x_c = \begin{vmatrix} v_{AB} \\ v_{AC} \\ v_{AD} \end{vmatrix}$$

The value of the determinant will be positive if the vector triplet define a right-handed set and will be negative if the triplet is left handed. The restraint maintains a particular value for this volume so that the refinement will resist deformation of the chiral group. Derivatives of these volumes are computed numerically by individually displacing each atom by 0.005 along each Cartesian axis in turn and recomputing the volume. The derivatives are then transformed to crystal coordinates before using to build the least squares matrix. These calculations are done in CHRCALC and CHVOLM. The chiral volume restraints are edited in subroutine EDTCHIR.

Coupled torsion angle pseudopotential restraints

The coupled torsion angle pseudopotential term uses 2-dimensional Gaussians to represent a pseudopotential energy surface for the steric interference between side chains associated with a pair of adjacent torsion angles (Von Dreele, J. Appl. Cryst., 34, 1084-1089, 1999). The function is

$$R_c = A_0 + \sum_{i=1}^{n} A_i \, exp\left[-B_i(\phi_{oi} - \phi_c)^2 - C_i(\varphi_{oi} - \varphi_c)^2 - D_i(\phi_{oi} - \phi_c)(\varphi_{oi} - \varphi_c) \right]$$

with a term for each potential well in the surface. A constant bias (A_o) is used to place the minimum in the pseudopotential at zero. The coefficients (A_i, B_i, C_i, D_i, ϕ_{oi}, and ψ_{oi}) are determined by the GSAS program RAMAFIT by fitting to experimentally observed torsion angles or known coupled torsion angle distributions. For example, four terms can be used to represent the well-known Ramachandran plot for protein ϕ-ψ torsion angles in a peptide chain. For the fit an energy score was assigned to each region of the Ramachandran plot (core=-3, allowed=-2, generous=-1 and disallowed=0). In this case, the values of ϕ_c,ψ_c are obtained from each amino acid in the protein (excepting glycine and proline) to calculate this contribution to the minimization function. Derivatives are computed numerically by displacing each atom by 0.005 along each Cartesian axis and recomputing the pseudopotential energy. This restraint is edited by the routine EDTRAMA and the function and derivatives are computed in RAMACALC.

Positive pole figure restraints

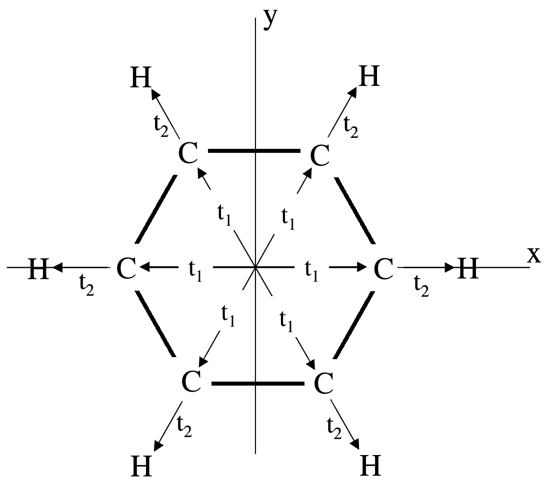
Because a pole figure gives a representation of the pole distribution probability, the values everywhere on a pole figure must be positive. This condition can be imposed on a selected set of pole figures during a Rietveld refinement of spherical harmonics texture coefficients. The general axis equation

$$z = 1 + \sum_{l=2}^{L} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \sum_{n=-l}^{l} C_l^{mn} k_l^m(h) k_l^n(y)$$

is used to compute the pole figure values for the points on a square grid (typically 24x24) that fall across the circular area of the pole figure. Those values that are negative are included and restrained to be zero; positive values are ignored. Derivatives are computed analytically. This restraint is edited by the routine EDTZPF and the function and its derivatives are computed in ZEROPF.

Rigid body calculations

A rigid body molecule in GSAS is described by a sequence of scaled translation vectors for the atoms in a local Cartesian coordinate system. For example, a benzene ring can be built by two translations for the six carbon atoms and the six hydrogen atoms starting from the centroid of the molecule.



In the first step the six C atoms and six H atoms are translated by t_1 along the vectors (1,0,0), (cos60,sin60,0), (-cos60,sin60,0), (-1,0,0), (-cos60,-sin60,0), (cos60,-sin60,0). For the second step only the H atoms are translated by t_2 along these vectors. The two translations used in this case are refinable parameters in GSAS, and this model preserves the D_{6h} symmetry of the benzene molecule. Alternative descriptions are possible in which the group is built by a different sequence of translation scales and vectors from a different choice of origin that gives a different flexibility to the model. For example, the C_6H_5 phenyl group may be built from the C atom that forms the attachment point with a sequence of four translations that follow the bonding pattern and allow the three types of C-C bond lengths and the C-H bond length to be refined separately. In more general terms the position of any atom, X=(X,Y,Z), in a rigid body is given by

$$X = \sum_{i=1}^{N_t} t_i v_i$$

where the t_i are the translation scalars and v_i are the associated vectors. Up to fifteen individual rigid body groups each containing up to 500 atom each may be defined in GSAS and each rigid body can be built from up to fifteen individual translation scalar/vector combinations.

The rigid body is then oriented in preparation for inclusion within the crystallographic unit cell by a sequence of up to six rotations. These are defined as rotations of the coordinate system about the Cartesian axes {X,Y,Z}.

$$R_x(\alpha_1) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha_1 & -\sin\alpha_1 \\ 0 & \sin\alpha_1 & \cos\alpha_1 \end{pmatrix}$$ for a rotation α_1 about the X axis

$$R_y(\alpha_2) = \begin{pmatrix} \cos\alpha_2 & 0 & \sin\alpha_2 \\ 0 & 1 & 0 \\ -\sin\alpha_2 & & \cos\alpha_2 \end{pmatrix}$$ for a rotation α_2 about the Y axis

$$R_z(\alpha_3) = \begin{pmatrix} \cos\alpha_3 & -\sin\alpha_3 & 0 \\ \sin\alpha_3 & \cos\alpha_3 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$ for a rotation α_3 about the Z axis

The order and number of these rotations is selected by the user to properly orient the group within the crystal structure. Although only three rotations at most are required for any conceivable molecular orientation, an additional three are provided to allow ìpreorientationî of a group so that a refined rotation can occur about some ìnaturalî direction in the crystal structure. At most three of these rotations are refinable in GSAS; crystallographic symmetry may limit this to less than three. The rigid body coordinates then transform by

$X'=R_a(\alpha_6)R_a(\alpha_5)R_a(\alpha_4)R_a(\alpha_3)R_a(\alpha_2)R_a(\alpha_1)X$ where a is one of X,Y or Z.

The coordinates of oriented rigid body group are then transformed to the crystallographic coordinate system defined by the unit cell axes {a,b,c} and then the origin of the group is translated to the appropriate location within the unit cell. Given the crystal to Cartesian transformation matrix

$$L = \begin{pmatrix} a & b\,cos\gamma & c\,cos\beta \\ 0 & b\,sin\alpha^*\,sin\gamma & 0 \\ 0 & -b\,cos\alpha^*\,sin\gamma & c\,sin\beta \end{pmatrix}$$

the rigid body atom locations in the crystal structure are given by

$x=L^{-1}$Xí+t

The location coordinates of the rigid body origin, $t=(x_t,y_t,z_t)$, are refinable in GSAS as limited by symmetry. A given rigid body may be placed at up to fifteen different locations within the crystallographic unit cell. Each rigid body placement has the associated six rotations and three translations available for positioning. The set of atom coordinates must contain a contiguous set of atoms defined for the set of atoms in each rigid body that is inserted into the structure and no atom may reside in more than one rigid body.

Anisotropic thermal motion of the atoms within a rigid body can be represented by using the TLS convention. The T(ëtranslationí), L(ëlibrationí) and S(ëscrewí) thermal motion matrices are

$$T = \begin{pmatrix} T_{11} & T_{12} & T_{13} \\ T_{12} & T_{22} & T_{23} \\ T_{13} & T_{23} & T_{33} \end{pmatrix},\ L = \begin{pmatrix} L_{11} & L_{12} & L_{13} \\ L_{12} & L_{22} & L_{23} \\ L_{13} & L_{23} & L_{33} \end{pmatrix} \text{ and } S = \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix}$$

Note that T and L are symmetric and S is not. The thermal motion tensor for each atom with respect to the rigid body Cartesian coordinate system is

$U_i=T+A_iS+S^TA_i^T+A_iLA_i^T$

where

$$A_i = \begin{pmatrix} 0 & Z_i & -Y_i \\ -Z_i & 0 & X_i \\ Y_i & -X_i & 0 \end{pmatrix}$$

This thermal motion tensor is transformed to the anisotropic thermal parameters, u_{ij}, used in GSAS by

β=gUg and then $u_{ij} = \beta_{ij} \big/ \sqrt{g_{ii} g_{jj}}$

where g is the reciprocal metric tensor defined above for computing reflection d-spacings. Since the three diagonal elements for the S tensor cannot be determined independently, they are combined to two terms, $S_{AA}=S_{33}-S_{11}$ and $S_{BB}=S_{22}-S_{33}$. The TLS description for the thermal motion of a rigid body has six T tensor elements (T_{11}, T_{22}, T_{33}, T_{12}, T_{13} and T_{23}), six L tensor elements (L_{11}, L_{22}, L_{33}, L_{12}, L_{13} and L_{23}) and eight S tensor elements (S_{12}, S_{13}, S_{21}, S_{23}, S_{31}, S_{32}, S_{AA} and S_{BB}) for a total of 20 parameters. Local symmetry at the rigid body site may limit the number of TLS coefficients required for a given problem.

Derivatives of the crystallographic parameters of the atoms within the rigid body (positions and anisotropic thermal parameters) with respect to the rigid body parameters are evaluated and placed in the appropriate terms in the rigid body constraint matrix, R_{il}, which is used *via* the chain rule to reduce the parameter derivative vector to the variable derivative vector (see below). Rigid body groups are constructed and placed by routine EDTRGBD, input and output in GENLES are done by RGBDINP and RGBDOUT, and calculations are done by RGBDCAL.

Least Squares Calculations

To minimize M by least squares, a set of derivatives of the individual functions (e.g. F_c^2, I_c, d_c) 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

$$\sum_{h=1}^{N_h} w_h \left(F_{ho}^2 - SF_{hc}^2\right)\frac{\partial F_{hc}^2}{\partial v_i} + \sum_{p=1}^{N_p} w_p \left(I_{po} - I_{pc}\right)\frac{\partial I_{pc}}{\partial v_i} + f_d \sum_{r=1}^{N_r} w_r \left(d_{ro} - d_{rc}\right)\frac{\partial d_{ro}}{\partial v_i} + ! \quad = 0$$

where the sums are over all the types of observations. The first sum is for single crystal observations, the second for powder pattern observations and the third and succeeding sums for stereochemical restraints. After expansion as a Taylor series and ignoring the high order terms, the set of observational equations becomes

$$Ax = y$$

where the vector is constructed from each contribution by

$$y_i = \sum_{h=1}^{N_h} w_h \Delta\left(F_h^2\right)\frac{\partial F_h^2}{\partial v_i} + \sum_{p=1}^{N_p} w_p \Delta\left(I_p\right)\frac{\partial I_p}{\partial v_i} + f_d \sum_{r=1}^{N_r} w_r \Delta\left(d_r\right)\frac{\partial d_r}{\partial v_i} + !$$

$$x_i = \Delta v_i$$

and

$$a_{ij} = \sum_{h=1}^{N_h} w_h \frac{\partial F_{hc}^2}{\partial v_i}\frac{\partial F_{hc}^2}{\partial v_j} + \sum_{p=1}^{N_p} w_p \frac{\partial I_p}{\partial v_i}\frac{\partial I_p}{\partial v_j} + f_d \sum_{r=1}^{N_r} w_r \frac{\partial d_r}{\partial v_i}\frac{\partial d_r}{\partial v_j} + !$$

These equations are linear in the Δv_i and can be solved by inverting the symmetric matrix A by

$$A^{-1}Ax = A^{-1}y$$

$$x = A^{-1}y = By$$

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

$$B_{ij} = \frac{B'_{ij}}{\sqrt{A_{ii}A_{jj}}}$$

and

$$x_i = \frac{x'_i}{\sqrt{A_{ii}}}$$

The inverse matrix B is then used to obtain the variance-covariance matrix by normalizing by the reduced χ^2.

$$\sigma_i^2 = \frac{B_{ii}^2}{\chi^2}$$

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 esdís apply to the variables themselves and proper error propagation through the constraint matrices is used to obtain the esdís for the set of parameters.

Since the crystallographic least-squares problem is not linear, convergence is achieved only after repeating several cycles of refinement. In GENLES the convergence is monitored by examining the following sum

$$S = \sum_{i=1}^{N_v} \left({}^{\Delta v_i}\!/_{\sigma_i} \right)^2$$

over the variables in the refinement. By default if S is less than 0.01 then the refinement is considered to be ëconvergedí and GENLES will stop. This criterion can be changed by the user.

For very large refinement problems (i.e. proteins) GSAS uses an approximation to the full matrix in which only those terms that fall into a band about the diagonal are considered. All other terms are zero. Consequently special band matrix techniques are used for inversion and solution, but the sequence of operations is what is given above for the full matrix approach.

These calculations in GENLES are performed by MATSLV and a set of subroutines called by it for matrix normalization (MATSCL), inversion (LSSS or LSSSB 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 ëEXPNAM' option of the main GSAS command procedure. This name must be given by the user before beginning work on the 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

The first file produced by the system is the main data and control file, expnam.EXP. Each record in this file is 80 characters long and starts with a 12-character key that is used to fetch that record from the file; the information on that record is read in fixed format. For the MS-DOS and Unix versions of GSAS, this process is performed by routines within GSAS; the file itself is in direct access fixed length record 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 in the file 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 UPDATE 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, ëcí. The data are flags controlling distance and angle calculation limits and inclusion of data from a peak search of Fourier maps.

```
('  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.

```
('  GNLS SHFTS',2F10.2) BIGSESD,AVESESD
```

The values of the largest Δ_v/σ_v and the average Δ_v/σ_v for the variables in the last least squares refinement cycle. This record is written by MATSLV in GENLES.

```
(' AFAC aaaa  ',9F7.0)(FFAC(I),I=1,9)
           a = element symbol
```

The first atom data record for atom type ëaí. 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. ëTI+4í; 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 ëAFACí 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

(' AFAC aaaa N',9F7.0,F5.0)(NFFAC(I),I=1,9),GFAC
           a = element symbol
```

These two records are present only when a magnetic form factor is available for the chosen element or ion. Data in table 4.4.5.1 of International Tables for X-ray Crystallography, Vol. C, has been 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, EXPEDT can read a file containing the scattering factor data as a function of $\sin\theta/\lambda$ and fit it to the needed function in subroutine EDTMFF. The first record contains the coefficients for the <j0> form factor and the second record contains the coefficients for the <j2> form factor. The LandÈ g-factor, GFAC, depends on the amount of spin-orbit coupling for the ion.

```
(' AFAC aa_nnn',F7.0,4F6.0)MASS,BLEN,RNMU,RNMUX
```

The isotopic data for ëaa_nnní where ëaaí is the chemical symbol (upper case) and ënnní is the isotope. The data are isotopic weight, real neutron scattering length, and the wavelength dependent and wavelength independent neutron absorption cross-sections. If ënnní is blank then the data are for the natural abundance element. Synthetic elements do not have ënatural abundanceí data. This record also has the following form.

```
(' AFAC aa_nnn', F7.0,2F6.0,F7.0,6F6.0) MASS,BLEN,(BFAN(I),I=1,8)
```

If columns 77-78 of this record are not blank then this alternate form is used. It contains the coefficients for computing the wavelength dependent neutron real and imaginary scattering lengths.

```
(' 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. CPK style colors are chosen for many of the elements. The colors are used by both ORTEP and VRSTPLOT.

```
(' 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 Kα 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, C: constant wavelength or E: x-ray energy dispersive) and the status of the data set (blank: use in least squares, D: dummy powder histogram not processed by GENLES, R: read powder histogram, X: powder profile not processed by POWPREF or *: do not use in least squares). The status flags F,G, I and N are used by the LANSCE SCD data processing programs. Thus the flag ëPNT ë means that this histogram is neutron TOF powder data that can be used in a least-squares refinement. Each type of restraint has its own special histogram type: ëRSN ë is used for bond lengths, ëANG ë for bond angles, ëBMP ë for van der Waals and hydrogen bonds, ëCHI ë for chiral volumes, ëFLT ë for planar groups, ëRAM ë for coupled torsion angle pseudopotentials, ëCMP ë for unit cell contents and ëZPF ë for pole figures. 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 36 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 restraint data.

```
(' EXPR ATYPnn',2X,A8,I5,2F10.0,F5.2,I5)
              n = 1,NATYP          TYPE,NATOM,DRAD,ARAD,PRAD,COLOR,HRAD
```

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 ëaasv_nnní where ëaaí is the chemical symbol, ësí is the valence sign (+ or -), ëví is the valence (typically 1-6) and ënnní 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 ëAFACí records for this atom type are not deleted. The atom radii are edited by EDTDIST and EDTBMP and read by DISAGL and BMPCALC in GENLES. The radii and colors are used by the graphics programs ORTEP and VRSTPLOT.

```
(' EXPR ftypRL',I10) LENREC
```

This record is written by FOURPRT4 within FOURIER and contains the length of records in the ëftypí Fourier map file. ëftypí is one of ëFOBSí, ëFCALí, ëDELFí, ënFDFí (n=2-9), ëPTSNí, or ëDPTNí. It is read by the Fourier map processing or plotting routines in preparation for opening the appropriate map file.

```
(' 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, 4 for macromolecular phase, or zero if the phase is absent. Only phase 1 may be a macromolecular phase. This record is updated by EDTPHAS and is read in many places in GSAS.

```
('REFN GDNFT  Reduced CHI**2 = cc.cccc     for   15 variables')
('REFN STATS  Cycleyyyy There were nnnnn observations.
                                   Total CHI**2 = s.ssssE+xx')
```

Refinement summary records. These are entered by RFCSOUT at the completion of each least squares refinement cycle in GENLES.

Crystal structure records

The next 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. It can be changed only by editing the phase information.

```
('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. If the chemical formula has not been entered then these records are absent. It is used by SCABS as the source of the absorption coefficient.

```
('CRSp   ATYPS',I5)NATYPS
```

Number of atom types for this phase; used to read the formula record, ëCRSp   FRMLc', shown below.

```
('CRSp   F000 ',2F10.0)FNEUT,FXRAY
```

The F_{000} scattering factors for neutrons and x-rays based on the chemical formula. This record is written by EDTCOMP and only appears if the chemical composition has been entered. The values are used by FOURIER.

```
('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. This record is written by EDTCOMP and used by SCABS.

```
('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 ëYí then the lattice parameters (as reciprocal metric tensor elements) will be refined from powder diffraction data. 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. The ëABCí and ëANGLESí records are first written by LATPARM, edited by EDTLAT and modified by CELLOUT in GENLES that also provides the ëSIGí records.

```
('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 ëmí; 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) = ëIí then UIJ(1) is U_{iso}, if CODE(1) = ëAí then six anisotropic u_{ij} values are given. If CODE(2) = ëFí then FRAC is to be refined; if CODE(3) = ëXí then XYZís are to be refined as permitted by symmetry; and if CODE(4) = ëUí then U_{iso} or the u_{ij}ís are to be refined as permitted by symmetry. These records are used for phase types NPHAS=1-3 and 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 ëmí, 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) = ëMí to refine these moment components as restricted by magnetic symmetry and IDAMP(4) is the damping factor to be applied as defined above. These records are used only for phase types NPHAS=2 or 3.

```
('CRSp  ATmmmm',2X,A8,F6.4,3F8.5,F6.4,A5,A3,A2,I4,6A1) ATYP,FRAC,
       X,Y,Z,UISO,NAME,RESNAME,GRP,RES,(CODE(I),I=1,3),(DAMP(I),I=1,3)
          m = 1 to NATOM (in hexadecimal)
```

Atom parameter record for atom ëmí in a macromolecular phase. It contains the atom type (matches one of the atom types given above), atom fraction, fractional coordinates, isotropic temperature factor, atom name, residue name, macromolecular chain identifier, residue number, refinement codes, and damping factors for FRAC, XYZ and UISO. The atom and residue names should conform to macromolecular naming conventions (e.g. CA for the C_α atom and PHE for phenylalanine). If CODE(1) = ëFí then FRAC is to be refined; if CODE(2) = ëXí then XYZís are to be refined as permitted by symmetry; and if CODE(3) = ëUí then U_{iso} is to be refined. These records are used only for phase type NPHAS=4 and are written by WRTPATM and read by REDPATM; the parameters are edited by several atom editing routines called from EDTPATM.

```
('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. It is only present for NPHAS=2 or 3 phase types.

```
('CRSp  ODF   ',2I5,I5,1X,4A1,2I5,3F10.4) NORD,NCOFF,ISAMSYM,
                                  IFREF,IDAMP,SANGL
```

Spherical harmonics texture control record. It contains the order of the harmonic to be used, the number of harmonic coefficients, sample symmetry flag, refinement flags, damping flags and the three sample orientation angles Ω_s, X_s and Φ_s. This record and the following ones are created by EDTPRFOH in EXPEDT. They are read and updated by ODFINP and ODFOUT in GENLES. Program POLFPLOT uses them to create and display pole figures.

```
('CRSp  ODFnnA',6(I4,2I3)) ((INDX(I,J),I=1,3), J=1,NCOFF)
('CRSp  ODFnnB',6F10.3) (COFF(I),I=1,NCOFF)
('CRSp  ODFnnC',6E10.4) (SIGM(I),I=1,NCOFF)
            n= 1 to (NCOFF-1)/6+1
```

Spherical harmonics texture coefficient records for this phase with six coefficients per record set. The first record contains the L, m and n indices for each C_L^{mn} term, the second record contains the value of the coefficient and the third contains the value of the esd from the least-squares refinement.

```
('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 in EXPEDT.

```
('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 that 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 ëYí 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.

```
('CRSpe EXTSN ',I5,2X,3A,2X,3I1,4X,A)EXTTYP,IEXCOD,
                                        (IDAMP(I),I=1,3),IEXTTP
('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.

These records describe the crystal shape for use in absorption calculations in SCABS. Their use depends on the value of PTYPE in the following ë`CRSpe PTYPE`í record.

`('CRSpe CHPHnn',3F10.4)CH,PH,DIST`

If PTYPE is ëPHI,CHI,í then this ëCHPHí form is used to describe each crystal face where ëCHí is χ and ëPHí is ϕ for the face in the reflecting position and DIST is the distance of the face from some arbitrary origin in the crystal.

`('CRSpe DCOSnn',4F10.4)COSA,COSB,COSC,DIST`

If PTYPE is ëDIRCOS,Dí then this ëDCOSí form is used to describe each crystal face where COSA, COSB, and COSD are the direction cosines for the face and DIST is the distance of the face from some arbitrary origin in the crystal.

`('CRSpe HKLDnn',4F10.4)H,K,L,DIST`

If PTYPE is ëH,K,L,D í then this ëHKLDí form is used to describe each crystal face where HKL are the Miller indices for the face and DIST is the distance of the face from some arbitrary origin in the crystal.

`('CRSpe PNTSnn',9F7.3)X1,Y1,Z1,X2,Y2,Z2,X3,Y3,Z3`

If PTYPE is ë3 POINTSí then this ëPNTSí form is used to describe each crystal face where X1-Z3 are the coordinates of three points on the face; typically these are the coordinates of three of the face vertices.

They are all written and edited by EDTPLNS in EXPEDT.

`('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 *a*-axis are coincident if PTYPE=ë3 POINTSí 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.

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 ëHAPí.

```
('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 single crystal 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 ë`HAPphhPREFOn'` (see below) records to be 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,
             n=1,NAXIS                                  DAMP,TYPE
```

This record gives the March-Dollase preferred orientation coefficient, direction, refinement code, damping factor for preferred orientation axis ënı́, and preferred orientation function type. The number of these records is determined from the ëHAPphhNAXIS ' (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.

```
('HST hh  HFIL',2X,A66)RAWNAM
```

The raw data file name that is the source of this histogram. This name uses whatever name the user had entered to describe this file at the time the file was introduced to experiment by EXPEDT for powder data or by CAD4RD, P3R3DATA or SXTLDATA 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 title record for single crystal data.

```
('HST hh  IFIL',2X,A66)INSTNAM
```

The file name of the instrument parameter file associated with this histogram.

```
('HST hh IRAD ',I5)IRAD
```

This is an integer (1 to 5) indicating which characteristic radiation (Cr, Fe, Cu, Mo or Ag K_{α}, 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,F10.4,2(4X,A1))NREF,DMIN,IFFOS,IFFCS
('HST hhMNREF ',I5,F10.4)MNREF,DMIN
```

The number of reflections in the reflection file for this histogram, the minimum d-spacing and a flag for powder data indicating whether F_o^2ís 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 IFFOS and IFFCS flags are set by PDCALC to ëYí after it has produced F_o^2ís and F_c^2ís and placed them in the reflection file. The MNREF record contains the number of magnetic reflections and the minimum d-spacing for them.

```
('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 are 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 ë`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 that are used for spherical harmonics texture analysis of polycrystalline samples. They are defined in the section ëPreferred Orientation of Powders: Spherical Harmonics Functioní above. These records are written by HSTCHG and read by ODFINP in GENLES and POLFPLOT.

Powder histogram records

Most of this information that 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 detector bank or scan number for the diffractometer.

```
('HST nn BIGFO ',G15.6)BIGFO
```

The largest value for F_o^2 extracted for any phase from this powder histogram. This value is determined by REFLIN and the record is written by PDCALC. It is used in REFLIST to produce the I_{100} table.

```
('HST hh CHANS',6I10)HOLDOFF,ICLMP,NCHANS,CHEKHST,MCHANS,ISAMP
```

The HOLDOFF for the first channel in the output powder histogram from POWPREF, 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 by POWPREF and GENLES. NCHAN is the number of channels desired, BINTYP is either ëCONSí or ëLOG6í and BCOEF includes the holdoff for the first channel and either the step size or the clock increment.

```
('HST hh EPHAS',9I5,4X,A1,I5) (EPHAS(I),I=1,9),IFFOS,DAMP
```

Flags to control the extraction of integrated intensities for the reflections in the histogram. If IFFOS is ëYí then F_o^2ís will be extracted from the powder pattern. The damping is used for LeBail type extractions. 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 fraction POLA, the polarization type IPOLA, and the $K_{\alpha2}/K_{\alpha1}$ ratio KRATIO are 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 MFIL ',A)INSNAME
```

The name of an incident spectrum file. The data points in this file must be arranged to match those in the histogram raw data file. I.e. they must use exactly the same neutron TOF time bin structure or CW 2Θ step size structure. This file is used as the source of the incident spectrum if the value of ITYP on the `'HST hhI ITYP'` record below is 10.

```
('HST hh NEXC ',I5)NEXC
```

The number of excluded regions in the pattern. There are 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, 4 for a macromolecular phase (only for phase 1), or zero if the phase is absent from this histogram. This record is updated by EDTHPHAS and is read in many places in GSAS.

```
('HST hh R-FAC',A,I5,A,F8.5)'N-obs',NREF,'R-factor',RFSQ
```

The number of reflection F_o^2ís extracted from this histogram and the value of R_F^2. This record is written by RFCSOUT and is used by GSAS2PDB for an entry in the powder diffraction template.

```
('HST hh RPOWD',2F10.4)RWP,RP
```

The weighted and unweighted profile residuals for this histogram. This record is output by PDCALC and is used by GSAS2PDB for an entry in the powder diffraction template.

```
('HST hh TRNGE',2F10.5)TMIN,TMAX
```

The first and last points in the histogram used in the refinement. The values are given in msec for neutron TOF, degrees for CW experiments or keV for x-ray energy dispersive experiments. It is written by HSTPROC and used by POWPLOT and GSAS2PDB. It is also used by BACKCAL and CALCBAK for computing function #1 (Chebyschev series).

```
('HST hh WREXP',F10.4)WREXP
```

The expected weighted profile residual for this histogram. This record is written by HSTPROC in POWPREF.

```
('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. This record originated from the instrument parameter file.

```
('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. It is also used for spherical harmonics texture calculations. It may be either a positive or negative value depending on which side of the diffractometer the detector bank is located. 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 hhDFUS  ',2I5,4X,A)NDIF,IDAMP,IFABS
```

The diffuse scattering function record. It contains the number of diffuse scattering terms, damping flag and a flag for the application of the powder absorption correction. It and the following record are created by EDTDFUS and used by DFUSINP and DFUSOUT.

```
('HST hhDFUSnn',I5,3F10.5,2X,3A1)TRMTYP,DIF(I),I=1,3),(IREF(I),I=1,3)
            n=1,NDIF
```

These records contain the individual diffuse scattering term type (1,2 or 3), the coefficients A,R and U and the individual refinement flags.

```
('HST hhEXCeee',2F10.3)(EXCM(I),EXCX(I),I=1,NEXC)
            e = 1 to NEXC
```

The excluded regions from EXCM to EXCX in msec, degrees 2Θ or keV; 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 is the product of this scale and the ëHAPí 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. At least the first two records are required for every powder histogram. These data are defined by the program FITSPEC. All of these are read by HSTPROC in EXPEDT 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 and maximum over which the function can be applied and a checksum on the incident spectrum. The minium and maximum are given in the appropriate units for the powder pattern (i.e. TOF in msec, 2Θ in degrees or energy in keV). The checksum is used to check if this incident data has been applied to another histogram. If ITYP is 10 then the incident spectrum is read point-by-point from a separate file given on the `'HST hh  MFIL'` record shown above. the

```
('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 or ten these records are not needed.

```
('HST hhIECOFc',4E15.6)(SINC(I),I=1,12)
             c = 1 to 3
```

The σís for each of the coefficients. If ITYP above is zero or ten 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 σís are used to calculate the σ in the calculated incident intensity at each point in the profile. If ITYP above is zero or ten 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 reflection 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 ëHAPí 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 a later section.

```
('HST hh  INST',I5)INSTNO
```

Record pointing to the appropriate instrument parameter records.

```
('HST hh CDAT1', '2X,A4,2X,A8,1X,L1,3F6.3)DATASRC,ABSTYPE,PRTREF,
                                            SHPRAD,ERRINS,DSMAX
```

Histogram dependent control data for SCABS. DATASRC is the radiation type (i.e. ëCuKaí for CuK_α), ABSTYPE is the absorption correction type (i.e. ëPSI-SCANí), PTREF is a logical controlling the printing of reflections by SCABS, SHPRAD is the sphere radius in mm, ERRINS is the instrument error constant (typically = 0.01) 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 wavelength 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 ìEXPNAMî.Mhh 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 h00 lattice row for the crystal as mounted on a single crystal goniometer. They are written by CAD4RD, P3R3DATA or

SXTLDATA and used in SCABS to calculate to orientation matrix in preparation for absorption corrections.

```
('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 ëmí. 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 hhPSIINT',F10.5)PSIINT
```

Interval in degrees for the ψ-scan. Written by PSISCNDTA in CAD4RD and read 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 ëmí. 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 hhREFLEN',I5)REFLEN
```

This record gives the length of the records in the single crystal data reflection file.

```
('HST hhTRNSLM',2E15.6)TRMX,TRMN
```

The maximum and minimum values for the transmission (absorption^{-1}) for this histogram as computed by SCABS that writes this record.

Restraint histogram records

All restraint histograms contain certain records in common. These follow below.

```
('HST hh  HNAM',2X,A66)HNAM
```

A histogram title entered by the user for the particular restraint histogram.

```
('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 restraints in this histogram on the refinement. Typical values for FACTR are 0.1-3.0.

Bond distance restraints

This histogram consists of expected interatomic distances with esdís. The histogram type is ëRSNë.

```
('HST hh NBNDS',I5)NBNDS
```

The number of interatomic distances for this histogram.

```
('HST hh RMSD  ',I5,F10.4)NBNDS,RMSD
```

The resulting root-mean-square difference between the set of expected distances and those calculated from the atomic positions.

```
('HST hhBDnnnn',I3,2I5,5I3,2F6.3)
                    IPHAS,AT1,AT2,ISYM,ILATT,IA,IB,IC,DIST,ESD
              n = 1,NBNDS (in hexadecimal)
```

The expected interatomic distance with esd from atom AT1 to AT2 after application of symmetry operator number ISYM, the lattice translation number ILATT and the unit cell translations IA, IB and IC. These records are edited in EDTBND and read by BNDCALC.

Bond angle restraints

This histogram consists of expected bond angles with esdís. The histogram type is ëANGë.

```
('HST hh NANGS',I5)NANGS
```

The number of bond angles for this histogram.

```
('HST hh RMSD  ',I5,F10.4)NANGS,RMSD
```

The resulting root-mean-square difference between the set of expected bond angles and those calculated from the atomic positions.

```
('HST hhANnnnn',2I5,2F10.2,3Z4)
                    IPHAS,NATOM,ANGLE,ESD,AT1,AT2,AT3
              n = 1,NANGS
```

The expected bond angle with esd from atom sequence AT1-AT2-AT3. No symmetry operators are applied, thus it is expected that all three atoms are within close bonding distance of each other. These records are edited in EDTANG and read by ANGCALC.

van der Waals and hydrogen bonding restraints

This histogram consists of expected non-bonded minimum interatomic distances and selected hydrogen bonding distances with esdís. The histogram type is ëBMPë.

```
('HST hh FACTR',2G15.6)FACTR,FACTRH
```

The multiplier for the contributions from this histogram to the minimization function. The first one is for the van der Waals contact distances and the second is for the hydrogen bonds. These can be used to control the influence of the restraints in this histogram on the refinement. Typical values for FACTR are 0.1-3.0.

```
('HST hh RMSDB ',I5,F10.4)NBMPS,RMSD
```

The number of close contacts and their root-mean-square difference between the set of expected van der Waals contacts and those calculated from the atomic positions. Only those distances less than the sum of the van der Waals radii are counted.

```
('HST hh RMSDH ',I5,F10.4)NHBNDS,RMSD
```

The resulting root-mean-square difference between the set of expected hydrogen bond distances and those calculated from the atomic positions. The number of hydrogen bonds found is also given. These records are edited in EDTBMP and read by BMPCALC.

Chiral volume restraints

This histogram consists of expected chiral volumes with esdís. The histogram type is ëCHI ë.

```
 ('HST hh NCHIR',I5)NCHIR
```

The number of chiral volumes for this histogram.

```
('HST hh RMSD ',I5,F10.4)NCHIR,RMSD
```

The resulting root-mean-square difference between the set of expected chiral volumes and those calculated from the atomic positions.

```
('HST hhCHnnnn',2I5,2F10.2,4Z4)
                  IPHAS,NATOM,VOLUME,ESD,AT1,AT2,AT3,AT4
             n = 1,NCHRS
```

The expected chiral volume with esd from atom vector triplet AT1-AT2, AT1-AT3 and AT1-AT4. If the triplet forms a right handed set then the chiral volume is positive, if it is left handed then the volume is negative. The restraint can be defined either way. No symmetry operators are applied, thus it is expected that all four atoms are within close bonding distance of each other. These records are edited in EDTCHR and read by CHRCALC.

Planar group restraints

This histogram consists of expected planar groups with esdís. The histogram type is ëFLTë.

```
('HST hh NPLNS',I5)NPLNS
```

The number of planar groups for this histogram.

```
('HST hh RMSD  ',I5,F10.4)NPLNS,RMSD
```

The resulting root-mean-square displacement of all the atoms from their respective planes. The number of atoms in all planes is also given.

```
('HST hhPLnnnn',2I5,F5.2,12Z4)
                  IPHAS,NATOM,ESD,(AT(I),I=1,NATOM)
             n = 1,NPLNS
```

The esd on the individual atom displacements from the best plane formed from the atom sequence AT(1)-AT(NATOM). A maximum of 12 atoms can comprise a plane. No symmetry operators are applied, thus it is expected that all atoms are within close bonding distance of each other. These records are edited in EDTPLN and read by FLTCALC.

Torsion angle restraints

This histogram consists of expected bond torsion angles with esdís. The histogram type is ëTORë.

```
('HST hh NTORS',I5)NTORS
```

The number of bond torsion angles for this histogram.

```
('HST hh RMSD  ',I5,F10.4)NTORS,RMSD
```

The resulting root-mean-square difference between the set of expected bond torsion angles and those calculated from the atomic positions.

```
('HST hhTOnnnn',2I5,2F10.2,3Z4)
                  IPHAS,NATOM,TORSION,ESD,AT1,AT2,AT3,AT4
             n = 1,NTORS
```

The expected bond torsion angle with esd from atom sequence AT1-AT2-AT3-AT4. No symmetry operators are applied, thus it is expected that all four atoms are within close bonding distance of each other. These records are edited in EDTTOR and read by TORCALC.

Coupled torsion angle pseudopotential restraints

This histogram consists of expected bond angles with esdís. The histogram type is ëRAMë.

```
('HST hh ETRMn ',6F10.3)(ETERM(I),I=1,6)
             n=1,NTRMS
```

The coefficients (A,ϕ,ψ,B,C,D) for one term in the coupled torsion angle pseudopotential.

```
('HST hh NRAMS',2I5) NRAMS,NTRMS
```

The number of coupled torsion angles and the number of pseudopotential terms for this histogram.

```
('HST hh RMSD  ',I5,F10.4)NRAMS,RMSD
```

The resulting root-mean-square difference between the set of expected bond angles and those calculated from the atomic positions.

```
('HST hhRAnnnn',2I5,2F10.2,5Z4)
                  IPHAS,NATOM,ESD,AT1,AT2,AT3,AT4,AT5
             n = 1,NRAMS
```

The esd for the pseudopotential from atom sequence AT1-AT2-AT3-AT4-AT5. No symmetry operators are applied, thus it is expected that all five atoms are within close bonding distance of each other. These records are edited in EDTRAM and read by RAMCALC.

Positive pole figure restraints

This histogram consists of a selection of pole figures that are expected to be positive with esdís. The histogram type is ëZPFë.

```
('HST hhZPF   ',2I5)NPF,NGRID
```

The number of pole figures to examine for negatives and the number of grid points to use for the search.

```
('HST hhZPF  n',4I5,F10.3,I5,F10.4)IPHAS,H,K,L,ZESD,ZNUM,ONESD
             n=1,NPF
```

The phase and hkl for the pole figure to be searched to be positive within the esd of ZESD. ZNUM is the number of negative grid points found on the map. If ONESD is positive then an additional restraint is imposed that all pole figure values be unity with an esd of ONESD. These records are edited in EDTZPF and read by ZEROPF.

Unit cell contents restraints

This histogram consists of expected unit cell contents with esdís. The histogram type is ëCMPë.

```
('HST hh NCMPS',I5)NCMPS
```

The number of unit cell contents restraints for this histogram.

```
('HST hh CMP n ',I5,2F10.5)NTRMS,CMPSUM,CMPESD
             n=1,NCMPS
```

The number of terms in this restraint, the unit cell sum expected and the esd on that value.

```
('HST hh CMP nm',3(2I5,F10.5))(IPH(I),ISEQ(I),CMULT(I),I=1,NTRMS)
              m=1,(NTRMS-1)/3+1
```

The phase number, atom sequence number and atom fraction multiplier for one term in the unit cell contents restraint. These records are edited in EDTCMP and read by CHEMCMP.

Single crystal instrument data records

The following records characterize the single crystal diffractometer used in the experiment.

```
('INST  NINSTS',I5)NINSTS
```

The number of single crystal instrument descriptions used in this experiment file. Currently GSAS is limited to a single instrument description for such instruments so that ënní in the following records is ë 1í.

```
('INSTnn  IFIL',2X,A66)
```

Name of the instrument parameter file that was read into this experiment.

```
('INSTnn NAME ',2X,A66)NAME
```

A title entered in the instrument parameter file to provide further identification of the file.

```
('INSTnnATTNww',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.

```
('INSTnnCHIR  ',F10.5)CHIR
('INSTnnOMGR  ',F10.5)OMGR
('INSTnnPHIR  ',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 ìupî). 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.

Constraint records

The next set of records contains 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 cccc   ',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 ëABS1í, ëABS2í, ëBKnn í, ëDIFA í, ëDIFC í, ëDUFAí, ëDUFRí, ëDUFUí, ëEXTP í, ëFP c í, ëFPPc í, ëFS1í, ëFS2í, ëHSCL ë, ëLAM1 í, PFnn ëë, POLA í, ëPRFO í, ëPSFRí, ëRMij ë, ëSCAL í, ëTTH ë, ëKRAT ëand ëZERO ë.

```
('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 ëhí) or phases and histograms (as ëp,hí) whose overall parameters ëccccí are to be constrained and VALUE is the coefficient. Allowed strings for ëpí and ëhí are ëaí for a single histogram or phase, ëa:bí for a sequence from ëaí to ëbí where ëaí and ëbí are integers and ëALLí for all histograms or phases. For example ë2:4,ALLí refers to phases 2 through 4 for all histograms. In the case of ëRMijí constraints, CONSTR is the character string ëp RMijí, where ëpí is the phase number and ëijí 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 ëhí 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 ëpí 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 ëpí 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. The atom number is represented in hexadecimal form. The atom parameter names are ëFRACí, ëXí, ëYí, ëZí, ëUISOí, ëU11í, ëU22í, ëU33í, ëU12í, ëU13í, ëU23í, ëMXí, ëMYí and ëMZí for non-macromolecular phases and ëFRAí, ëXí, ëYí, ëZí and ëUISí for a macromolecular phase.

ORTEP records

The records that are next are written by ORTEP and hold the last set of atoms and bonds to be drawn by that program for phase ëpí.

```
('ORTp   NATOM',I5)NATOM
```

The number of atom designator codes to be found on the ë`ORTp   ATMSnn'` records.

```
('ORTp   NBOND',I5)NBOND
```

The number of bond descriptor records to be found on the ë`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 ëaaacccssí is composed of three parts; the first, ëaaaí, is an atom serial number, the second, ëcccí, is the unit cell designators along a,b and c for the location of the atom and the third, ëssí, 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 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
       n=1,NRBDS (in hexadecimal)
```

The number of atoms in rigid body ënί.

```
('RGBD n NBDS ',I5)NBDS
       n=1,NRBDS (in hexadecimal)
```

The number of times this rigid body is used in all phases.

```
('RGBD n NSMP ',I5)NSMP
       n=1,NRBDS (in hexadecimal)
```

The number of translation vectors needed to build the rigid body.

```
('RGBD nmPARM ',F10.5,2I5)SDIST,IVAR,IDAMP
        m = 1,NSMP, n=1,NRBDS (both in hexadecimal)
```

The magnitude of the translation vector ëmί, the variable number in the least-squares matrix and damping flag. The variable number can be either unique or the same as another translation vector magnitude in which case they will be taken as the same least squares variable. This variable number is selected by the user.

```
('RGBD nmSCiii',3F10.7)TRX,TRY,TRZ
             i = 1,NATR and m = 1,NSMP (both in hexadecimal)
```

The translation vector on Cartesian xyz axes for atom ëiί, these are multiplied by SDIST from the associated ë`RGBD nmPARM` ί 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
       n=1,NRBDS (in hexadecimal)
```

The number of times rigid body type ënί occurs in phase ëpί.

```
('RGBDpnr  NDA',I5)NDA
       n=1,NRBDS; r=1,NBDS (both in hexadecimal)
```

The atom sequence number for the first atom of rigid body ërí. All atoms in a rigid body are stored in the experiment file in sequential locations. There must be ëNATRí atoms in the atom list with serial numbers in sequence starting with ëNDAí. These atoms cannot 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)
       n=1,NRBDS; r=1,NBDS (both in hexadecimal)
```

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. These variable numbers are user selected.

```
('RGBDpnr BDLC',3F10.7)BDLOC(I),I=1,3)
       n=1,NRBDS; r=1,NBDS (both in hexadecimal)
```

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)
       n=1,NRBDS; r=1,NBDS (both in hexadecimal)
```

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
       n=1,NRBDS; r=1,NBDS (both in hexadecimal)
```

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 ëCRSp   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)
       n=1,NRBDS; r=1,NBDS (both in hexadecimal)
```

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 that 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)
       n=1,NRBDS; r=1,NBDS (both in hexadecimal)
```

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 ^{2}, the L matrix elements are in degrees^2 and the S matrix is in degree- .

SCD instrument records

These records are unique to the TOF neutron single crystal diffractometer at the Lujan Center, Los Alamos National Laboratory (SCD instrument). They are generally not used by any of the distributed parts of GSAS. The routines referred to here are part of the local data processing routines that use the GSAS formalism for experiment file records. These are listed here as these records may appear in experiment files produced for this instrument.

```
('  FNDP CDATc',2I5) NPEAKS,MININT
('  FNDP HDATc',15A4) (LHST(I),I=1,M)
           c = 1 to 9(max)
```

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/σ(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 that are to be added to the current data before integrating. 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, ìRESTî or ìALLî, or a number.

```
(' 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 that 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.

```
('HST hh NREFF',I5)NREFF
```

The number of reflections found by FINDPK in this histogram. This is the number in the ìEXPNAMî.Rhh reflection file.

```
('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 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 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.

```
('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 number of events recorded 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 scalar 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 and all other programs that process raw SCD data.

```
('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 that were used to collect this histogram. The data record is written by REDHST and is read by HSTPLOT that 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 define the shape of the histogram. The data are the range of neutron wavelengths 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.

```
('INSTnn 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.

```
('INSTnn RDATE',2X,A66)
```

Date and time of the last instrument parameter refinement.

```
('INSTnnBCHI  ',2F10.3)BCHI,SIGBCHI
('INSTnnBDETA ',2F10.3)BDETA,SIGBDETA
('INSTnnBDETD ',2F10.3)BDETD,SIGBDETD
('INSTnnBOMGA ',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.

```
('INSTnnCHID  ',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.

```
('INSTnnDETA  ',2F10.3)DETA,SIGDETA
('INSTnnDETD  ',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.

```
('INSTnnFILTYP',2X,A8)FILTYP
```

The flag differentiating the various SCD data formats. There are four file formats that are recognized by the LANSCE SCD codes. Three LANSCE formats and one ANL format

```
('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.

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 (notably 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.

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.tnn - The Reflection Files

These are files that contain a set of reflections for each histogram entered in the experiment file. The filename extension contains the histogram number ënní and a letter ëtí indicating the type of reflection information in the file. For powder data ëtí is ëPí, for single crystal data ëtí is ëSí, for FINDPK output reflections ëtí is ëFí and for merged (FINDPK is a routine for searching local Los Alamos SCD raw data sets and is not part of the standard GSAS package) single crystal data ëtí is ëMí. 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 (ëtí is ëSí) all 36 data items in the following list are used, for merged (ëtí is ëMí) only the first 22 items are used and for FINDPK data (ëtí is ëFí) 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 ìstandard indicesî
= 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 ëMí type files are opened, read and written by the ëS' routines.

EXPNAM.Phh - The Histogram Files

There is a histogram file ëEXPNAM.Phhí 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 ìrecordî consists of

ICODE	profile point status code
T	time of flight in µsec or 2å 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 ìrecordsî are entered into an array by WRITPRF; when full the block is written to the histogram file. Similarly, the ìrecordsî are read from the array by READPRF; if a requested ìrecordî 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 four large logical records each of which is described below.

```
NCYCLE,NUMPAR,(PARNAMS(I),I=1,NUMPAR),NUMVAR,(VARNAMS(I),I=1,NUMVAR),
   SUMDSQ
```

The first logical record contains the least squares cycle number, the number of refinable parameters and their names, the number of resulting least squares variables and their names and the value of the minimization function, M. 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,MBW,(AMAT(I),I=1,MATSIZ)
```

The second logical record contains the size of the variance-covariance matrix, the band matrix width (zero if full 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.

```
(PVALUE(I),I=1,NUMPAR)
```

The fourth logical record contains the resulting values of all the parameters varied in the refinement. They are in the same order as the PARNAMS given in the first record.

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, nFDF (n=2 to 9 where the map density is computed from nF_o-$(n-1)F_c$), PTSN and DPTN that 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 consist of two header records followed by a set of data records, one for each map ësliceí.

```
PHASNAM,DESCR,MAPTYP
```

The first header record contains 66-character phase name and title, and the map type (FOBS, etc.) as a 4-character code (also used for the extension. 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,
                                 TRHOX,TRHON,SRO
```

The second header gives the number of steps along the cell edges, the starting step position, the number of steps computed, an orientation flag, the number of density values per slice, the maximum map density, the minimum map density and the sum of density values over the whole 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. If NRHO is larger than 8191 then multiple records are written for each section each with 8191 items. Only the last of these records will have ROMX and ROMN.

NAME.rfl – Output Reflection File

The GSAS program REFLIST can optionally produce a file containing reflection information from a selected phase for a particular powder histogram. The ìNAMEî is arbitrarily chosen by the user. The file format is designed for use by SIRPOW and MULTAN directly; the latter program will require a ìFORMATî command to specify the format. Each record contains

```
(3I4,I8,F10.7,2F10.3,F10.0,F10.1,F10.4,I4,F10.3)
                              IHKL,MUL,STOL,TTH,FWHM,FOSQ,SIG,FOBS,ID,PHAS
```

where IHKL are *hkl*, MUL is the multiplicity, STOL is the value of $\sin\Theta/\lambda$, TTH is the 2Θ (or TOF) position of the reflection, FWHM is the full width at half maximum of the reflection, FOSQ is F_o^2, SIG is an estimate of σF_o^2, FOBS is F_o, ID is set to 0 for reflections with $F_o^2>0$ and 1 otherwise, and PHAS is the reflection phase angle. The error is arbitrarily estimated from

$$\sigma F_o^2 = 0.025 F_o^2 + 1.0$$

The file is terminated by

```
(3I4,58X,F10.4,I4) 0,0,0,-100.0,1
```

that is expected by MULTAN.

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,A)IBANK,NCHAN,NREC,BINTYP,(BCOEF(I),I=1,4),TYPE
```

The fields are separated by spaces and ëBANKí 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 correspond to the bank number found in the instrument parameter file for the detectors that 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. If TYPE is blank or ëSTDí, there are 10 data points per record so NREC is NCHAN/10 rounded up. If TYPE is ëESDí then NREC is NCHAN/5 rounded up and there are 5 data points per record. If TYPE is ëALTí there are 4 data points per record and NREC is NCHAN/4 rounded up. The value of BINTYP depends on the way the step-widths are determined. The ëSTDí 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 cannot be obtained in this way, then one of the other data formats that explicitly input the esd should be used (see below).

If TYPE is ëSTDí or blank then the powder profile is read as NREC records 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. Note that it is permissible to enter the intensities without the decimal point, hence each field can contain an intensity value up to 999999. If the measured intensities are greater than this one should scale down the data and use one of the other input formats that enter the values for the esd for each profile point.

If TYPE is ëESDí 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. This format should be used if the observed counts are scaled or corrected for any systematic effects. This includes the scaling by incident intensity commonly done for synchrotron data. X-ray powder data obtained from image plates should also use this format with a realistic estimate of the esd for each point.

If TYPE is ëALTí then the data records also include the position of each point in somewhat unusual units. The form 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 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 intensity and YE is the esd for YOT. Normally the decimal point is left off the values and the format statement properly scales the values.

The BINTYP flag on the ëBANKí record above can have several different values depending on the algorithm used to determine the values of the independent variable used to collect the diffraction pattern.

If BINTYP is ëCONDí then the diffraction data was collected with a constant step width in d-spacing. The value of BCOEF(1) is the starting value of the d-spacing, BCOEF(2) is the size of the step in d-spacing from one step to the next and BCOEF(3) is the radiation wavelength used in the data collection. BCOEF(4) is zero and ignored. This information is used by GSAS to convert the data point positions to 2Θ.

If BINTYP is ëCONSí then the diffraction data was collected with a constant step width. The value of BCOEF(1) is the value for the first data point and BCOEF(2) is the size of the step to each succeeding data point. BCOEF(3) and BCOEF(4) are zero and ignored. For CW data the units assumed by GSAS are in centidegrees (0.01), μsec for neutron TOF data and keV for x-ray energy dispersive data.

If BINTYP is ëCONQí then the diffraction data was collected with a constant step width in Q(=2π/d). The value of BCOEF(1) is the value of Q for the first data point, BCOEF(2) is the size step in Q to each succeeding data point, and BCOEF(3) is the wavelength of the radiation used to collect the data. BCOEF(4) is zero and ignored. This information is used by GSAS to convert the data point positions to 2Θ.

If BINTYP is ëEDSí then the diffraction data was collected in nominally constant steps in x-ray energy in keV. The BCOEF(1)-BCOEF(4) are the coefficients of a simple power series relating step number to X-ray energy and are determined from calibration during the data collection.

If BINTYP is ëLOG6í 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 step size increment for the Los Alamos Model 6 TOF clock. BCOEF(3) and BCOEF(4) are zero and ignored. This BINTYP is probably obsolete.

If BINTYP is ëLPSDí then the data is assumed to be in constant intervals across the face of a linear position detector or image plate. BCOEF(1) is the nominal 2Θ value in centidegrees for the 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. BCOEF(4) is zero and ignored. This information is used by GSAS to convert the data point positions to 2Θ.

If BINTYP equals ëRALFí then the data was collected at one of the TOF neutron diffractometers at the ISIS Facility, Rutherford-Appleton Laboratory. The width of the time bins is constant for a section of the data at small values of TOF and then varies (irregularly) in pseudoconstant ΔT/T steps. 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).

If BINTYP is ëSLOGí then the neutron TOF data was collected in constant $\Delta T/T$ steps. BCOEF(1) is the initial TOF in μsec, and BCOEF(3) is the value of $\Delta T/T$ used in the data collection. BCOEF(2) is a maximum TOF for the data set. BCOEF(4) is zero and ignored.

If BINTYP equals ëTIME_MAPí 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.

A time map suitable for neutron TOF data collected at Los Alamos 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 ëTIME_MAPí 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 that 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. The time map is usually positioned at the head of the data file just after the title and ëInstrument parameterí record and is followed by data sets for the various banks of detectors on the TOF instrument. 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.) is stored on a formatted sequential file. Each record is 80 characters long and starts with a 12-character key describing the type of information on the record. The information on the record is read as a 66-character block by TYPINS and written unchanged on to the ëAFACí records in the experiment file. The file is arranged so that all information for a given element is in one place on eight different kinds of records; the elements are arranged in atomic number order. 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 nn')
   z=atomic number; nn=number of records that follow
```

This record begins a block of records for an element.

```
('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. ëTI+4í, 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.

```
('zz aaaa M',9F7.0)(MFFAC(I),I=1,9)
        a = element symbol

('zz aaaa N',9F7.0,F5.0)(NFFAC(I),I=1,9),GFAC
        a = element symbol
```

These two records are present only when a magnetic form factor is available for the chosen element or ion. Data in table 4.4.5.1 of International Tables for X-ray Crystallography, Vol. C, has been used as listed for the elements and ions in that table. The first record contains the coefficients for the <j0> form factor and the second record contains the coefficients for the <j2> form factor. The LandÈ g-factor, GFAC, depends on the amount of spin-orbit coupling for the ion.

```
('zz aa_nnn   ',F7.0,4F6.0)WT,BLEN,BILEN,RNMU,RNMUX
```

The isotopic data for ëaa_nnní where ëaaí is the chemical symbol (upper case) and ënnní is the isotope. The data are isotopic weight, real neutron scattering length, and the wavelength dependent and wavelength independent neutron absorption cross-sections. If ënnní is blank then the data are for the natural abundance element. Synthetic elements do not have ënatural abundanceí data. There may be several of these records for a given element. The values are taken from Koster & Yelon, (1982), Neutron Diffraction Newsletter. This record also has the following form.

```
('zz aa_nnn   ', F7.0,2F6.0,F7.0,6F6.0) MASS,BLEN,(BFAN(I),I=1,8)
```

If columns 77-78 of this record are not blank then this alternate form is used. It contains the coefficients for computing the wavelength dependent neutron real and imaginary scattering lengths.

```
('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. In many cases the COLOR is chosen to approximate one of the CPK colors.

```
('zz aa_XAB   ',1X,5F6.0)(RXMU(I),I=1,5)
```

The x-ray absorption cross sections for Cr, Fe, Cu, Mo and Ag K_α 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 (fí and fî) of the anomalous dispersion for Cr, Fe, Cu, Mo and Ag K_α 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-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 distribution kit for GSAS has many examples of these files in \gsas\example. 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 characterizes the whole instrument and is 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   HTYPE ',2X,A4)HTYPE
```

The histogram type for all data from this instrument; see the description of the ë EXPR HTYPcí record in an experiment file for a full description of histogram types. For powder data the last character of HTYPE must be ëRí; the other characters specify the kind of data. This record is required by GSAS.

The next section of records contains specific information for a bank of detectors or for one kind of CW scan. They are repeated for each of the NBANK detectors or scan types 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 $K_{\alpha 2}/K_{\alpha 1}$ 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 K_{α}, 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 bb MFIL ',A)INSNAME
```

The name of an incident spectrum file. The data points in this file must be arranged to match those in the histogram raw data file. I.e. they must use exactly the same neutron TOF time bin structure or CW 2Θ step size structure. This file is used as the source of the incident spectrum if the value of ITYP on the `'INS bbI ITYP'` record below is 10.

```
('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 ìdummyî 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 esdís 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 esdís 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.

The following are instrument parameter records required for a single crystal instrument. See \gsas\example\cad4.prm. for an example of one of these.

```
('INST   NAME ',2X,A66)NAME
```

A title entered to identify the instrument.

```
('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  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 ìupî). 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.