Mathematical Basis

Introduction

In this section of the technical manual we describe the mathematical functions used in **GSAS** for the computation of various quantities and indicate the principal locations of the associated algorithms in the code. The routine names are in bold face.

Structure Factors

The structure factors, $F_{p,h}$, for both single crystal and powder data are computed in the standard way from atomic coordinates, atom form factors and temperature factors and the same expressions are used for both x-rays and neutrons. For the powder case, there is a set for each phase (p) in each histogram (h). The expression is the usual complex quantity

$$F_{p,h} = A_{p,h} + iB_{p,h}$$

where A and B are the cosine and sine parts of the structure factor (see below). If the structure is centrosymmetric and the inversion center is located at the unit cell origin then B is zero. Because of this simplifying process the space group routines in **GSAS** always place the inversion center at the origin. Since the observed intensity is related to the square of this quantity, the expression

$$F_c^2 = A^2 + B^2$$

is calculated for all diffraction data. Given that the atomic X-ray form factors also include anomalous dispersion contributions and are modified by atomic site fraction (x) and the thermal motion correction (T" - see below)

$$f = xT''(f_o + f' + if'')$$

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

$$A = A_o + A' - B''$$

$$B = B_o + B' + A''$$

where

$$A_o = \sum_i x_i T''_i f_{oi} \mathit{cos} 2\pi \mathbf{h}\cdot\mathbf{r} \qquad B_o = \sum_i x_i T''_i f_{oi} \mathit{sin} 2\pi \mathbf{h}\cdot\mathbf{r}$$

$$A' = \sum_i x_i T''_i f'_i \mathit{cos} 2\pi \mathbf{h}\cdot\mathbf{r} \qquad B' = \sum_i x_i T''_i f'_i \mathit{sin} 2\pi \mathbf{h}\cdot\mathbf{r}$$

$$A'' = \sum_i x_i T''_i f''_i \mathit{cos} 2\pi \mathbf{h}\cdot\mathbf{r} \qquad B'' = \sum_i x_i T''_i f''_i \mathit{sin} 2\pi \mathbf{h}\cdot\mathbf{r}$$

and the sums are over the unit cell contents. For neutrons the expressions are the same except that the form factors are generally just real scattering lengths (b_o). A few elements and isotopes show anomalous scattering so

$$f = xT''(b_o + ib')$$

In the powder case the averaging process means that the intensity for a single reflection includes contributions from Friedel reflection pairs. Thus the above components must be differently combined for the single crystal case to represent the powder intensity

$$F^2 = (A_o+A')^2 + B''^2 + (B_o+B')^2 + A''^2$$

In **GSAS** the atomic coordinates, site fractions and thermal motion parameters are refinable quantities. In addition, the anomalous dispersion contributions (f' and f") for X-rays are also refinable.

The temperature factors are expressed as either U_{iso} or u_{ij} where the thermal correction to the structure factor is either

$$T'' = e^{-(8\pi^2 U_{iso} \sin^2\Theta/\lambda^2)}$$

for isotropic thermal motion or

$$T'' = e^{-[2\pi^2(u_{11}h^2a^{*2} + . . . + 2u_{12}hka^*b^* + . . .)]}$$

for anisotropic thermal motion. Alternative forms for the temperature factors which may be more familiar are B_{iso} and β_{ij} where

$$B_{iso} = 8\pi^2 U_{iso}$$

and

$$\beta_{ij} = 2\pi^2 a_i^* a_j^* u_{ij}$$

The structure factors and their derivatives for x-rays and nuclear scattering of neutrons are calculated by subroutine **STRFCTR** for both powder and single crystal data.

Additionally, neutrons may also be scattered by ordered magnetic moments on some of the atoms in a crystal structure. In **GSAS** we assume that the neutron beam is unpolarized, i.e. the neutron spins are randomly oriented with respect to the diffraction vector. Thus, the total diffracted intensity is a simple sum of the nuclear and magnetic scattered intensities

$$F^2 = F^2_{nuc} + F^2_{mag}$$

The structure factor for magnetic scattering depends on both the magnitude of the magnetic cross section (p) and the magnetic interaction vector (**q**). Thus the structure factor is

$$\mathbf{F}_{mag} = \sum_i \mathbf{q}_i p_i e^{2\pi i \mathbf{h}\cdot\mathbf{x}_i}$$

which is a vector quantity and the sum is taken over all the magnetic atoms in the unit cell. Since there is no polarization, the magnetic scattered intensity is simply the square of the magnitude of $\mathbf{F}_{mag}$. The magnetic cross section is a function of the magnitude of the magnetic moment (S) and the magnetic form factor (f_m) for the magnetic atom

$$p = 0.54Sf_m \times 10^{-12}\ \mathrm{cm}$$

and the magnetic interaction vector for the j^{th} atom depends on the unit vector (ε) for the scattering vector (**h**) and the unit vector for the magnetic moment on that atom($\mathbf{K}_j$)

$$\mathbf{q}_j = \varepsilon(\varepsilon\cdot\mathbf{K}_j)-\mathbf{K}_j$$

Magnetic structure factors and derivatives are calculated in **MAGSTRFCTR**.

Atom input and output in **GENLES** is handled by the subroutines **ATMSINP** and **ATMSOUT**, respectively. There are several atom editing routines all called by **EDTATM** in **EXPEDT**. The X-ray anomalous dispersion coefficients are edited as overall parameters by **EDTFFAC**.

Total Powder Diffraction Profile Intensity

The total normalized profile intensity, I_o, at any point in a powder diffraction pattern has contributions from the nearby reflections and from background scattering. The reflection contributions are calculated from the structure factors and are corrected for all geometric and sample dependent factors such as absorption, extinction, preferred orientation, etc. The background is modeled with a well behaved empirical function. The general expressions for the intensity of TOF data are

$$I_o = \frac{I'_o}{WI_i}$$

or for CW data

$$I_o = \frac{I'_o}{I_i}$$

and

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

where I'_o is the number of counts observed in a channel of width W, I_i is the incident intensity, I_b is the background value, S_h is the histogram scale factor, $S_{p,h}$ is the individual phase scale factor within an histogram and $Y_{p,h}$ is the contribution from the h^{th} reflection of the p^{th} phase. The two scale factors are useful for the analysis of multiphase mixtures. A weight, w, is assigned to each I_o from consideration of the variances in both I'_o and I_i. The sum is over those reflections from all phases in the sample that are sufficiently close to the profile point to make a significant contribution. Each of the terms in this expression will be discussed below. The computation of the total intensity and final assembly of its derivatives is done in subroutine **PDCALC**.

Incident Intensity Function

The incident intensity, I_i, for a time of flight (TOF) powder diffractometer can be measured by placing a null coherent scatterer such as vanadium in the normal sample position and then recording the spectrum observed by each of the counter banks. Alternatively, the incident spectrum can be obtained from a low efficiency beam monitor. Usually these spectra are used without correction for absorption or detector efficiency to determine the incident intensity. The lack of a detector efficiency correction in the neutron TOF case is exactly compensated because the powder diffraction data from a sample is collected with the same set of detectors. The lack of an absorption correction is compensated largely by the refinement of the sample absorption factor (see below). The incident intensity for a TOF diffractometer is represented by one of five possible functions each with a maximum of 11 or 12 coefficients. Only three of these functions are suitable for synchrotron x-rays; however, the usual procedure is to normalize synchrotron data point-by-point before processing by **GSAS** and not use the fitted incident intensity (see the section on **GSAS Standard Powder Data File**). These coefficients are determined by fitting to the measured incident spectrum; this is done by the program **FITSPEC**. It writes to an instrument parameter file the coefficients, estimated standard deviations (esd's) and the correlation matrix from a least squares fit. **POWPREF** uses this information to calculate the incident intensity and its esd for every point in a powder diffraction pattern. This esd is used to adjust the weight assigned to each profile point for the uncertainty in the calculated incident intensity.

The 'TYPE 1' function is a sum of exponentials of TOF (T) in milliseconds or 2Θ in degrees.

$$I_i = P_1 + P_2 e^{-(P_3 T)} + P_4 e^{-(P_5 T^2)} + \ldots$$

This function has a maximum of 11 coefficients. The 'TYPE 2' function replaces the second term in the above function with a Maxwellian expression; again TOF is in milliseconds. This function is not suitable for x-rays.

$$I_i = P_1 + P_2 e^{-(P_3/T^2)}/T^5 + P_4 e^{-(P_5 * T^2)} + \ldots$$

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

$$t = \frac{2.374 \times 10^{-4} C^2}{P_3 \sin 2\Theta}$$

where C is the diffractometer constant (DIFC). This temperature is usually 10-20K higher than the real temperature when the intensity data has not been corrected for absorption or detector efficiency. The 'TYPE 3' function is a 12 term Chebyschev polynomial of the first kind ("Handbook of Mathematical Functions," M. Abramowitz and I.A. Stegun, Eds., Ch. 22).

$$I_i = \sum_{j=1}^{12} P_j T'_{j-1}$$

where T'_{j-1} are the coefficients of the Chebyschev polynomial taken from Table 22.3, p 795 of the Handbook. Each coefficient is of the form

$$T'_n = \sum_{m=0}^{i-1} C_m X^m$$

and the values of C_m are listed in the Handbook. These coefficients are generated in subroutine **IFUNADV**. The TOF or $2\Theta(T)$ is converted to X to make the Chebyschev polynomial orthogonal by

$$X = (2/T) - 1$$

Given that the usual range of TOF is 1 to 100 millisec and 2Θ is from 2˚ to 175˚ then X ranges from about -1 to +1 which is the orthogonal range for this function. The 'TYPE 4' incident intensity function has a Maxwellian term and part of the Chebyschev polynomial used for 'TYPE 3'. It is not used for x-rays.

$$I_i = P_1 + \frac{P_2}{T^5} e^{-(P_3/T^2)} + \sum_{j=4}^{12} P_j T'_{j-3}$$

Again T is TOF in milliseconds and T'_i are the coefficients of the Chebyschev polynomial of the first kind. The 'TYPE 5' function is the same as 'TYPE 3' except that X is defined as

$$X = T/10$$

The 'TYPE 3', 'TYPE 4' and 'TYPE 5' functions have a maximum of 12 coefficients. For constant wavelength data with no incident spectrum, a 'TYPE 0' incident spectrum is used and has no coefficients; this gives $I_i = 1.0$ for all data points and σI_o is taken only from I_o. The subroutine **HSTPROC** in **POWPREF** reads the incident spectrum parameters, computes the values by calling **INAWCAL** and places this information with the observed pattern on the histogram file. **INAWCAL** also provides the appropriate set of derivatives for use by **FITSPEC**. The histogram file is processed by **GENLES** using the subroutine **PDCALC**.

Background Functions

There are currently six background functions available in **GSAS** for fitting to powder diffraction data. Each function has a maximum of 36 possible coefficients although in vitrually all cases far fewer will suffice to fit the background in a powder pattern. In fact, an attempt to use a large number of background coefficients will usually fail in an unpredictable way. The first function is the 'Chebyschev polynomial of the first kind' and is similar to that used for the incident spectrum 'TYPE 3'. A conversion is applied it make the Chebyschev polynomial orthogonal:

$$X = \frac{2(T-T_{min})}{T_{max}-T_{min}} - 1$$

where T_{min} and T_{max} are the actual range of data used in the calculation. T is in milliseconds TOF or degrees 2Θ. Then the background intensity is calculated from

$$I_b = \sum_{j=1}^{36} B_j T'_{j-1}$$

The coefficients T'_j are the same as those for the 'TYPE 3' incident spectrum and the values of B_j are determined by least squares during the Rietveld refinement of the powder pattern. The second background function is a cosine Fourier series with a leading constant term.

$$I_b = B_1 + \sum_{j=2}^{36} B_j \cos\,(P(j-1))$$

In the case of CW data P is in degrees 2Θ and is just the detector position for the step. For TOF data the times are scaled by 180/TMAX, where TMAX is the maximum allowed by the incident spectrum. This function appears to be more robust than the Chebyschev function for both CW and TOF data and thus is chosen as the default.

The third function uses a straight line for the first part and the major features of a real space correlation function for the remainder. Thus this background function can model diffuse background from an amorphous phase in the sample or the background from a quartz sample holder. The function is

$$I_b = B_1 + B_2 T + \sum_{i=1}^{17} \frac{B_{2i+1} \sin\,(QB_{2i+2})}{QB_{2i+2}}$$

where

$Q = 2\pi/d$

The d-spacing is computed for each point from the TOF or 2Θ and the diffractometer constants (see below). The values of B_{2i+2} correspond to interatomic distances in the amorphous phase. To assist the user in estimating these values, **POWPLOT** has an option for plotting both the modified residuals and the correlation function from the profile deltas; the B_{2i+2} can be picked off the latter plot.

The fourth function is designed to account for background contributions that increase with Q. The principal contributor of this kind is thermal diffuse scattering so this function is an expansion of the exponential

$$I_b = \sum_{j=1}^{36} B_j \frac{Q^{2(j-1)}}{(j-1)!}$$

The fifth function accounts for background contributions that tend to rise at small Q. In x-ray scattering the principal contribution of this type is from air scatter in the vicinity of the sample. This function is assumed to be effectively the reciprocal of the previous one

$$I_b = \sum_{j=1}^{36} B_j \frac{(j-1)!}{Q^{2(j-1)}}$$

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

$$I_b = B_1 + \sum_{j=1}^{17} \left(B_{2j} \frac{Q^{2j}}{j!} + B_{2j+1} \frac{j!}{Q^{2j}} \right)$$

This function is generally useful for both x-ray and neutron powder data although it may require a few more terms to get a satisfactory fit to the background. All three of these latter functions use the same definition for Q that is used for the third function.

Except for function #3, these background functions are normally quite flat. There is usually only a slight curvature arising from the thermal diffuse scattering from the sample. Larger background contributions will be fitted by these functions given sufficient terms, but short period fluctuations not associated with an amorphous phase cannot be fit very well. In that case the fixed background subtraction feature of **GSAS** must be used for the fluctuating component of the background with the remainder fitted with one of these functions. Examples of background problems include frame overlap peaks in a TOF pattern, miscellaneous peaks from sources outside the experiment and unaccounted extra phases. In the case of extra Bragg peaks from other phases in the sample, it is better to insert the phase explicitly and fit it as part of the crystallographic model. Using too many background terms may seriously degrade the quality of some other parts of the least squares model. In particular refinement of atom thermal parameters and some profile shape parameters may become very unsatisfactory because a very complex background function may begin to model parts of the Bragg peak intensities. Thus it is best to use the minimum number of background terms that give a satisfactory fit. The background coefficients are edited by subroutine **EDTBAK** and the input, output and calculations in **GENLES** are done by **BACKINP**, **BACKOUT** and **BACKCAL**, respectively. The routine **CALCBAK** is used in **POWPLOT** for subtracting calculated background.

Bragg Intensity - $Y_{p,h}$

The contributed intensity, $Y_{p,h}$, from a Bragg peak to a particular profile intensity will depend on several things. Obviously the value of the structure factor and the amount of that particular phase will determine the total contribution. In addition, the peak shape and width in relation to its position will also have an effect. The intensity is also affected by extinction and absorption as well as some geometric factors.

$$Y_{p,h} = F^2_{p,h} H(T-T_{p,h}) K_{p,h}$$

where $F_{p,h}$ is the structure factor for a particular reflection, $H(T-T_{p,h})$ is the value of the profile peak shape function for that reflection at a position, T, displaced from its expected position, $T_{p,h}$, and $K_{p,h}$ is the product of the various geometric and other correction factors for that reflection. In **GSAS** all of the applicable correction factors are applied to the Bragg intensities so that the resulting scale factors are proportional to the number of unit cells of each phase present in the sample. Moreover, the corrections include the angular effects to produce scale factors in a TOF experiment that are independent of scattering angle. The reflection position independent information and associated derivatives for powder data are assembled by subroutine **REFLIN** and written to a 'window' array which is read by **PDCALC** as the profile points are processed.

Intensity Correction Factors

The intensity correction factors, $K_{p,h}$, consist of those factors which are dependent on the sample, the instrument geometry, and the type of radiation used.

$$K_{p,h} = E_{p,h}A_hO_{p,h}M_pL/V_p$$

where $E_{p,h}$ is an extinction correction, A_h is an absorption correction, $O_{p,h}$ is the preferred orientation correction, M_p is the reflection multiplicity, L is the angle dependent correction (Lorentz-polarization), and V_p is the unit cell volume for the phase. These corrections and their derivatives are assembled in **REFLIN** and are dependent only on the reflection. Each will be discussed in turn below.

Extinction in Powders

The extinction in powders is calculated according to a formalism developed by Sabine, Von Dreele and Jorgensen (T.M. Sabine, Aust. J. Phys., 1985, 38, 507-18 & T.M. Sabine, R.B. Von Dreele & J.-E. Jorgensen, Acta Cryst A44, 374-379, 1988) and is a primary extinction effect within the crystal grains. The extinction correction $E_{p,h}$ is a combination of Bragg and Laue components

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

where

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

and

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

or

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

where

$x = E_x(\lambda F/V)^2$

where F is the calculated structure factor and V is the unit cell volume. The units for these expressions are such that E_x is in μm^2 and is a direct measure of the mosaic block size in the powder sample. There is a value of the coefficient E_x for each phase in each histogram in a powder mixture. The powder extinction coefficients are input and output by **EXTPINP** and **EXTPOUT**, respectively; the function and its derivative are calculated by **EXTPCAL**. Editing is done in **EDTEXTP**.

Powder Absorption Factor

Several powder absorption functions are available in **GSAS**. In the first one, the absorption, A_h, for a cylindrical sample is calculated for powder data according to an empirical formula (A.W. Hewat, Acta Cryst., A35, 248, 1979 & K.D. Rouse, M.J. Cooper, & A. Chakera, Acta Cryst., A26, 682-691, 1970). It is assumed for TOF data that the linear absorption of all components in the sample vary with 1/velocity, and it is indistinguishable from multiple scattering effects within the sample. For constant wavelength data the absorption coefficient, A_B, is related to the value for 1Å neutrons; the correction is indistinguishable from thermal motion effects and should not be refined. For X-ray data it is suitable only for data taken in the Debye-Scherrer geometry on a weak absorber; it should not be used for Bragg-Bretano or other flat plate geometries.

$$A_h = e^{(-T_1 A_B \lambda - T_2 A_B^2 \lambda^2)}$$

where

$$T_1 = 1.7133-0.0368 \sin^2\Theta$$

and

$$T_2 = -0.0927-0.3750 \sin^2\Theta$$

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

$$A_h = e^{-A_B \lambda}$$

The third and fourth absorption functions are two forms for the surface roughness effect that is prevalent in Bragg-Brentano x-ray diffraction geometry. These two functions have two refinable coefficients, A_{B1} and A_{B2}. Surface roughness can strongly reduce the intensity of Bragg reflections at low scattering angles and is caused by a gradient in the sample packing density as a function of depth. Samples with high absorption are more susceptible to surface roughness effects and if not corrected can yield negative temperature factors in the crystal structure results. Function three is a "normalized" form of the function described by Pitschke, Hermann and Mattern (Powder Diffraction, 8,74-83, 1993).

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

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

$$A_h = \frac{A_{B1}+(1-A_{B1})e^{-A_{B2}/sin\Theta}}{A_{B1}+(1-A_{B1})e^{-A_{B2}}}$$

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

The absorption coefficients are input and output by **ABSCINP** and **ABSCOUT**, respectively; the function and derivative are calculated by **ABSCCAL**. Editing is performed by **EDTABS**.

Preferred Orientation of Powders

The preferred orientation correction, $O_{p,h}$, is the formulation of Dollase and March (Dollase, W.A. (1986). J. Appl. Cryst. 19, 267-272 and March, A. (1932). Z. Kristallogr. 81, 285-297). It is applicable for both needle and plate shaped crystals and is explicitly correct when the sample has cylindrical symmetry along the diffraction vector and is a reasonable approximation when the cylinder axis is perpendicular to the diffraction plane. Thus, it covers the two most common diffraction geometries for powder diffraction; Debye-Scherrer geometry as used in neutron diffraction and Bragg-Bretano geometry as used for most X-ray powder diffractometers. It is especially effective when the sample is rotated about the appropriate axis to ensure cylindrical symmetry. The refinable coefficient, R_o, gives the effective sample compression or extension along the cylinder axis due to preferred orientation. If there is no preferred orientation then R_o=1.0.

$$O_{p,h} = \sum_{j=1}^{n}(R_o^2 cos^2A_j+sin^2A_j/R_o)^{-3/2}/M_p)$$

where A_j is the angle between the preferred orientation axis and the reflection vector h_p. The sum is over the reflections equivalent to h_p. It is assumed that the preferred orientation axis for the sample lies either preferentially normal to the diffraction plane or coincident with the diffraction vector. The value of the coefficient will depend on both the diffraction geometry and the crystallite shape. If a cylindrical sample is used so that platy crystals would be expected to pack normal to the diffraction plane R_o will be greater than one. For a flat plate sample, platy crystals are expected to pack normal to the diffraction vector and R_o will be less than one. For needle-shaped crystals the reverse relationships for the value of R_o are obtained. A second form for the preferred orientation correction uses the March-Dollase formulation for a cylindrically symmetric distribution which is oriented to be parallel to the incident beam. For both functions, it is possible to define a set of multiple preferred orientations for each phase. Thus, each orientation has two coefficients, R_o and f_o; f_o is the fraction of crystallites that are associated with a particular orientation axis. The values of f_o are forced to sum to 1.0. The routines for input, output and calculation are **PRFOINP**, **PRFOOUT** and **PRFOCAL**, respectively. The editing is done by **EDTPRFO** and has facilities for selection of the preferred orientation axes as well as editing the coefficient and refinement flag.

Reflection Multiplicity

The reflection multiplicity, M_p, as determined by symmetry is computed when the reflection set is generated by **POWPREF** and is written on the reflection file along with the Miller indices and other relevant values associated with each reflection. The reflection generation is done by **REFGEN** and **REFGEN1** which produces the unique, space group allowed set of reflections for all possible 3-dimensional space groups.

Angle Dependent Corrections

The angle dependent corrections for powder diffraction include the Lorentz factor for both neutrons and x-rays and the polarization factor for x-rays. For TOF neutron data there is an additional factor for the variation of scattered intensity with wavelength. For TOF neutrons

$$L = d^4 \sin\Theta$$

for constant wavelength neutrons

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

and for x-rays there are three functions. The first is

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

the second is suitable for x-ray diffractometers with an incident beam monochromator in parallel geometry

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

and the third is for a diffracted beam monochromator also in parallel geometry

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

where P_h is a refinable polarization fraction defined for each x-ray powder histogram. These terms are calculated in **DIFSCAL**.

Profile Peak Shape Function

The contribution a given reflection makes to the total profile intensity depends on the shape function for that reflection profile, its width coefficients and the displacement of the peak from the profile position. The locations of the peak are given in microseconds of TOF or in centidegrees 2Θ. Discussion of these values is given first followed by details of the peak shape functions presently installed in **GSAS**.

Neutron Time of Flight

For a neutron time-of-flight powder diffractometer the relationship between the d-spacing for a particular powder line and its TOF is

$$T_{p,h} = \text{DIFC}\ d_p + \text{DIFA}\ d^2_p + \text{ZERO}.$$

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.

$$\text{DIFC} = 252.816 \cdot 2\mathit{sin}\Theta(L_1+\sqrt{L_2^2+L_3^2/16}\ )$$

where Θ is the Bragg angle, L_1 is the primary flight path, L_2 is sample to detector center distance and L_3 is the height of the detector; all distances are in meters. The units of DIFC are then µsec/Å. These coefficients are also slightly affected by the choice of profile function (see below). Precise values for constants DIFC, DIFA and ZERO must be obtained by fitting to a powder diffraction pattern of a standard material; this facility is available in **GSAS**. These coefficients are read by **GENLES** in subroutine **DIFSINP**, they are output by **DIFSOUT** and the calculation of the functions and derivatives is done by **DIFSCAL**. They are edited by subroutine **EDTDIF** in **EXPEDT**.

Neutron and X-ray 2Θ

The reflection position in a constant wavelength experiment is obtained from Bragg's Law.

$$\lambda = 2d_p\mathit{sin}\ \Theta$$

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

$$T_{p,h} = 200\mathit{asin}\ (\lambda_h/2d_p) + \text{ZERO}$$

In the case of neutron diffraction the **GSAS** system requires a single value for λ_h (called LAM1 in the code) and the ZERO value. This value of λ_h is obtained by fitting the powder pattern of a standard having a well known set of lattice parameters. For x-rays two values of λ_h can be used (called LAM1 and LAM2) along with the ZERO value. For conventional sources these wavelengths are well known and are tabulated in many references; however for synchrotron sources a calibration of the single wavelength with a standard sample can be performed. If both LAM1 and LAM2 are present they can not be refined. The intensity associated with LAM2 is normally assumed to be 1/2 the intensity of LAM1 in accord with theoretical expectations for K x-ray radiation emission from a laboratory source. However, this ratio (called KRATIO) can also be refined for those cases where the instrument optics have modified the $K\alpha_2/K\alpha_1$ ratio. The same routines in **EXPEDT** and **GENLES** that handle the TOF instrument parameters DIFC, DIFA and ZERO also handle LAM1, LAM2 and KRATIO.

Profile Functions

Each type of powder diffraction data has its own set of profile functions, $H[T-T_{p,h}]$; currently there are a small number installed in **GSAS** for each type of histogram which are discussed in turn. In all cases the input and output of the profile coefficients are done by **PRFCINP** and **PRFCOUT**, respectively. The calculations are grouped together in **PRFCCAL** which calls specific routines for each function. The editing is handled by **EDTPRF** which calls routines specific to the powder data type.

TOF Profile Functions

There are currently three TOF profile functions installed in **GSAS**. The first one is the function (J.D. Jorgensen, D.H. Johnson, M.H. Mueller, J.G. Worlton & R.B. Von Dreele, Proc. Conf. on Diffraction Profile Analysis, Cracow, 14-15 Aug., 1978, 20-22; R.B. Von Dreele, J.D. Jorgensen & C.G. Windsor, J. Appl. Cryst., 15 581-589, 1982; R.B. Von Dreele, unpublished).

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

where ΔT is the difference in TOF between the reflection position, $T_{p,h}$, and the profile point, T; the terms N,u,v,y and z are dependent on the profile coefficients. The function *erfc* is the complementary error function (see "Handbook of Mathematical Functions," Ch. 7). This profile function is the result of convoluting two back-to-back exponentials with a Gaussian.

$$H(\Delta T) = \int G(\Delta T-\tau)E(\tau)d\tau$$

where

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

and

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

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

$$G(\Delta T-\tau) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(\Delta T-\tau)^2/2\sigma^2}$$

The Gaussian variance is the coefficient σ^2. These functions when convoluted give the profile function shown above. The normalization factor, N, is

$$N = \frac{\alpha\beta}{2(\alpha + \beta)}$$

The coefficients u,v,y and z are

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

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

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

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

Each of the three coefficients α, β and σ^2 all show specific dependence on the reflection d-spacing. In the case of σ^2 there are terms for anisotropic broadening that depend on the angle ϕ between h_p and a broadening axis.

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

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

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

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

$$\Delta T = (T - T_{p,h}) - \varepsilon_i d - \varepsilon_a d\,\mathit{cos}\,\phi$$

Thus the profile function has twelve coefficients (α_o, α_1, β_o, β_1, $\sigma_o{}^2$, $\sigma_1{}^2$, $\sigma_2{}^2$, $\sigma_{oe}{}^2$, $\sigma_{1e}{}^2$, $\sigma_{2e}{}^2$, ε_i and ε_a) which are refinable by **GENLES**. Within **GSAS** these parameters are named "alp-0", "alp-1", "bet-0", "bet-1", "sig-0", "sig-1", "sig-2", "s0ec", "s1ec", "s2ec", "rstr" and "rsta", respectively. These parameters are sensitive to the scattering angle and any possible sample broadening effects; there is a set of these for each phase and each powder pattern.

The second TOF profile function has been developed by W.I.F. David and R.B. Von Dreele (unpublished) and incorporates the moderator pulse shape of S. Ikeda & J.M. Carpenter, Nuc. Inst. and Meth., A239, 1985, 536-544. The Ikeda-Carpenter function is composed of a convolution of two functions; the first represents the slowing down spectrum from the moderator

$$S_k(\tau) = \frac{\alpha^3}{2}\ \tau^2 e^{-\alpha\tau}$$

and the second is a mixing of a δ-function and an exponential decay:

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

The two parts describe the leakage of fast and slow neutrons from the moderator and have 'fast' and 'slow' decay constants, α and β, respectively, which are related to the moderator material and dimensions. The mixing coefficient, R, is related to the moderator temperature. The result of the convolution is

$$I_k(t) = \int S_k(\tau)R_k(t-\tau)d\tau$$

$$I_k(t) = \frac{\alpha^3}{2}\left[(1-R)t^2 e^{-\alpha t} + \frac{2\beta R}{(\alpha-\beta)^3}\left\{e^{-\beta t} - \left[1 + t(\alpha-\beta) + \frac{t^2}{2}(\alpha-\beta)^2\right]e^{-\alpha t}\right\}\right]$$

In **GSAS** an alternative form of this function is used to simplify some of the mathematics

$$I_k(t) = (1-R)\frac{\alpha(1-k^2)}{2k^2}\left[e^{-\alpha t(1-k)} + e^{-\alpha t(1+k)} - 2e^{-\alpha t}\right] + \frac{R\alpha\beta(1-k^2)}{2k^2}\left[\frac{2\alpha^2k^2}{xyz}e^{-\beta t} - \frac{1}{z}e^{-\alpha t(1+k)} - \frac{1}{x}e^{-\alpha t(1+k)} + \frac{2}{y}e^{-\alpha t}\right]$$

Where k is a perturbation coefficient (=0.05 in **GSAS**) and

$x = \alpha(1-k)-\beta$

$y = \alpha-\beta$

$z = \alpha(1+k)-\beta$

This function is convoluted with a pseudo-Voigt to give the full peak shape function

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

The pseudo-Voigt is defined as a linear combination of a Lorentzian and a Gaussian

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

The Gaussian function is defined above and the Lorentzian function is

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

The mixing factor, η, is given by P. Thompson, D.E. Cox & J.B. Hastings, J. Appl. Cryst.,20,79-83, 1987 as a function of the total FWHM (Γ) and the Lorentzian coefficient (γ)

$$\eta = 1.36603(\gamma/\Gamma) - 0.47719(\gamma/\Gamma)^2 + 0.11116(\gamma/\Gamma)^3$$

where Γ is a function of the Gaussian FWHM (Γ_g) and γ

$$\Gamma = \sqrt[5]{\Gamma_g^5 + 2.69269\ \Gamma_g^4\gamma + 2.42843\ \Gamma_g^3\gamma^2 + 4.47163\ \Gamma_g^2\gamma^3 + 0.07842\ \Gamma_g\gamma^4 + \gamma^5}$$

and the Gaussian FWHM is

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

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

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

or

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

and

$$h(g,r) = e^{\,(g+r^2)} erfc\,(r)$$

where

$$g = \frac{-\Delta T^2}{2\sigma^2}$$

$$r = \frac{\beta\sigma^2\text{-}\Delta T}{\sigma\sqrt{2}} \qquad s = \frac{\alpha\sigma^2\text{-}\Delta T}{\sigma\sqrt{2}}$$

$$u = \frac{\alpha(1\text{-}k)\text{-}\Delta T}{\sigma\sqrt{2}} \qquad v = \frac{\alpha(1+k)\text{-}\Delta T}{\sigma\sqrt{2}}$$

The Lorentzian part is also obtained by integration

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

or

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

where

$I(q) = Im[e^{\,q}E_1(q)]$ (i.e. imaginary part of $e^{\,q}$ times the exponential integral of q)

and

$p = -\alpha\Delta T + \frac{i\alpha\gamma}{2}$ $\quad$ $q = -\beta\Delta T + \frac{i\beta\gamma}{2}$

The profile coefficients are defined by

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

$$\beta = 1/\beta_o$$

$$R = e^{-(81.799/\kappa\lambda^2)}$$

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

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

This function currently has 15 parameters (α_o, α_1, β_o, κ, σ_o^2, σ_1^2, σ_2^2, γ_o, γ_1, γ_2, γ_{1e}, γ_{2e}, DIFC, DIFA and ZERO) and is still under development. DIFC is included to compensate for the offset in the peak location from that used for the first and third TOF functions. In this function the peak location is where the Ikeda-Carpenter function first rises from zero, i.e. at the front base of the profile. The other functions have the peak location at the junction between the exponentials, i.e. just to the low TOF side of the peak top. A weakness of this function is that it only suitable for data taken with very short detectors. Usually the detector banks are made up of a rank of ^{3}He tubes which are 6-12" long and the peak profile displays a sharp rise from the geometric effects from this tube length. The names of these coefficients within **GSAS** are "alp-0", "alp-1", "beta", "switch", "sig-0", "sig-1", "sig-2", "gam-0", "gam-1", "gam-2", "stec", "ptec", "difc", "difa", and "zero", respectively.

The third TOF profile function is an extension of the first function to include the generally Lorentzian broadening exhibited by most samples. Thus, the anisotropic broadening terms have been assumed to be Lorentzian. It is a convolution of the back-to-back exponentials used in the first function with the pseudo-Voigt used in the second function.

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

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

where N, u, v, y and z are defined as in the first function and p, q and η are defined as in the second function. The profile coefficients α, β and σ^2 are defined in ways similar to the two previous functions

$$\alpha = \alpha_1/d$$

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

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

For the γ profile coefficient an additional type of broadening is introduced where two classes of reflections can be defined. Those that fall on a sublattice (as defined by three vectors) have the following expression for the γ coefficient

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

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

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

This means that one set of reflections has a different particle size anisotropy than the other set. This effect is seen when the sample contains stacking faults which will broaden some reflections leaving a sublattice of sharp reflections which correspond to the substructure which continues unmodified through the stacking fault. Generally, γ_{2s} will be much larger than γ_{2e}. The sublattice is defined by three vectors chosen by the user via the profile function **'A'** option in **EDTPRF**. Thus, this function has 13 coefficients (α_1, β_o, β_1, σ_o^2, σ_1^2, σ_2^2, γ_o, γ_1, γ_2, γ_{2s}, γ_{1e}, γ_{2e}, ε_i and ε_a). These are named "alp", "bet-0", "bet-1", "sig-0", "sig-1", "sig-2", "gam-0", "gam-1", "gam-2", "gsf", "g1ec", "g2ec", "rstr", and "rsta", respectively, within **GSAS**.

The editing of the coefficients for all three functions is done by **EDTPTP1**. Calculations are handled through **PRFCCAL** which calls **EXPGAUS**, **IKCARVT** and **EXPSTVGT** for the three functions, respectively.

Interpretation of TOF Powder Profile Coefficients

The profile coefficients from a time of flight (TOF) neutron powder pattern Rietveld refinement with **GSAS** can give information about the microtexture of the sample. This discussion will describe how this information can be extracted from the coefficients.

Strain broadening

In the reciprocal space associated with a sample with isotropic strain, there is a broadening of each point which is proportional to the distance of the point from the origin, i.e.

$$\Delta d^*/d^* = \text{constant}$$

In real space (the regime of a TOF experiment) then

$$\Delta d/d = \text{constant}$$

for strain broadening. Thus examination of the expression for the Gaussian variance of the peak shape from a TOF pattern for the first function

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

implies that the second term contains an isotropic contribution from strain broadening. The other major contribution to σ_1^2 is from the instrument; because it is expressed as a variance, it can simply be subtracted. The remainder is then converted to give strain (S) as a dimensionless value which is frequently expressed as percent strain or fractional strain as a full width at half maximum.

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

where C is the diffractometer constant (DIFC) that relates TOF to d-spacing and $\sigma_{1i}{}^2$ is the instrumental contribution. In the case of anisotropic strain broadening, the parallel component of the strain is calculated from

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

The perpendicular component is then

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

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

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

indicates that strain should affect the second term. We assume that the instrumental contribution is Gaussian so no correction for an instrumental contribution is needed here

$$S = \frac{1}{C}\gamma_1\ 100\%$$

As above, the anisotropic strain can be determined from the two expressions

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

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

Particle size broadening

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

$$\Delta d^* = \text{constant}$$

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

$$\Delta d/d^2 = \text{constant}$$

From the expression for the Gaussian broadening of a TOF peak for the first function, the particle size affects the third term ($\sigma_2{}^2$) in the expression. This term generally has no instrument contribution and is used directly to calculate the particle size. Since it is in $\mu sec^2/Å^2$ 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 Å. The anisotropy in the particle size can also be determined relative to the broadening axis so that the parallel component is

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

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

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

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

In the presence of stacking faults, the γ_{2s} coefficient can be used to obtain the average distance between faults by

$$p_s = \frac{C}{\gamma_{2s}}$$

where the fault planes are perpendicular to the broadening axis.

As was noted for the strain, it has usually been observed that the particle size broadening is Lorentzian. Thus, it would appear that the third function would best fit diffraction data taken on high resolution TOF diffractometers with tall detectors.

CW Profile Functions

There are currently just two CW profile functions which are available for both x-rays and neutrons. The first function installed in **GSAS** is to be used for low resolution constant wavelength neutron powder diffraction data and is the standard Gaussian function modified for peak asymmetry, A_s, as described by Rietveld and others (H.M. Rietveld, J. Appl.

Cryst., 2, 65-71, 1969; Cooper & Sayer, J. Appl. Cryst., 8, 615-618, 1975; & Thomas, J. Appl. Cryst., 10, 12-13, 1977).

$$H(\Delta T) = N[1 - \Delta T'|\Delta T'|A_s/\mathit{tan}\ \Theta]e^{-\Delta T'^2/2\sigma^2}$$

the normalization factor, N, is

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

and the modified 2Θ difference is

$$\Delta T' = \Delta T + F_1/\mathit{tan}\ 2\Theta$$

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

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

Thus there are six profile coefficients U, V, W, A_s, F_1 & F_2 for constant wavelength neutron data; these are named "U", "V", "W", "asym", "F1", and "F2", respectively in **GSAS**. This function and its derivatives are calculated in **MODGAUS**, the coefficients are edited by **EDTPTP2**.

The second and considerably more successful function employs a multi-term Simpson's rule integration described by C.J. Howard (J. Appl. Cryst.,15, 615-620, 1982) of the pseudo-Voigt, F(ΔT), described by Thompson, et al. and used above in the second and third functions for TOF data.

$$H(\Delta T) = \sum_{i=1}^{n} g_i F(\Delta T')$$

where the pseudo-Voigt is

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

The mixing coefficient, η, and the FWHM, Γ, are defined above. The 2Θ difference modified for asymmetry, A_s, and sample shift, S_s, is

$$\Delta T' = \Delta T + f_i A_s/\mathit{tan}\ 2\Theta + S_s\mathit{cos}\ \Theta + T_s\mathit{sin}\ 2\Theta$$

where the number of terms in the sum depends on the size of A_s. The corresponding Simpson's rule coefficients, g_i and f_i, depend on the number of terms in the summation. In the case of Bragg-Bretano geometry for x-ray powder diffraction, the sample shift in can be interpreted as a physical shift of the sample, s, from the diffractometer axis by

$$s = \frac{-\pi RS_s}{36000}$$

where R is the diffractometer radius. In a similar way, the effective sample absorption can be obtained from the transparency coefficient, T_s, by

$$\mu_{eff} = \frac{-9000}{RT_s\pi}$$

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

$$\sigma^2 = U\mathit{tan}^2\Theta + V\mathit{tan}\,\Theta + W + P/\mathit{cos}^2\Theta$$

where U, V and W are the coefficients described by Cagliotti, Pauletti and Ricci in 1958 (Nucl. Instrum.,**3**, 223) and P is the Scherrer coefficient for Gaussian broadening. The Lorentzian coefficient, γ, varies as

$$\gamma = (X + X_e\mathit{cos}\,\phi)/\mathit{cos}\,\Theta + (Y + Y_e\mathit{cos}\,\phi)\mathit{tan}\,\Theta$$

The first term is the Lorentzian Scherrer broadening and includes an anisotropy coefficient, X_e. The second term describes strain broadening and also includes an anisotropy coefficient. If a sublattice is defined by use of "stacking fault vectors", then the above function only is applied to the reflections that are part of the sublattice. All other reflections have their Lorentzian broadening defined by (note the change from X_e to X_s)

$$\gamma = (X + X_s\mathit{cos}\,\phi)/\mathit{cos}\,\Theta + (Y + Y_e\mathit{cos}\,\phi)\mathit{tan}\,\Theta$$

This function gives the different anisotropic Scherrer broadening that is associated with the presence of stacking faults and is similar to that used in the #2 and #3 TOF functions shown above.

Thus there are twelve coefficients for this function (U, V, W, X, Y, T_s, A_s, S_s, P, X_e, Y_e and X_s). Within **GSAS** these are named "GU", "GV", "GW", "LX", "LY", "trns", "asym", "shft", "GP", "stec", "ptec", and "sfec", respectively. This function gives a better fit to asymmetric profiles than the first one and shows less correlation with the lattice parameters. The function and its derivatives are generated by **SIMGAUS**. The editing of the coefficients for these functions for neutron data are done in **EDTPTP2**. The coefficients for x-ray data are edited by **EDTPTP3**. The pairs of peaks arising from the $\alpha1$-$\alpha2$ doublet in the conventional x-ray case are treated as separate reflections.

Interpretation of CW Powder Profile Coefficients

As was the case for the TOF profile functions, the coefficients from a CW powder profile function can also be interpreted to give both strain and particle size information. Because the first function is suitable only for low resolution neutron CW diffractometers, it will rarely yield any significant line broadening information. Thus, the following discussion will consider only the coefficients from the second CW function.

Strain broadening

In the case of a CW experiment the strain broadening in real space is related to 2Θ broadening from

$$\Delta d/d = \Delta 2\Theta\,\mathit{cot}\,\Theta = \text{constant}$$

or

$\Delta 2\Theta = (\Delta d/d) \tan \Theta$

In this expression $\Delta 2\Theta$ is in radians. Examination of the expression for the Gaussian broadening

$\sigma^2 = U \tan^2\Theta + V \tan \Theta + W + P/\cos^2\Theta$

indicates that the first term contains a strain broadening component. As for the TOF expression, this is a variance and the instrument contribution can be subtracted off. This variance is in centideg^2 and must be converted to radians to yield strain, thus

$$S = \frac{\pi}{18000}\sqrt{8 \ln 2(U - U_i)}\ 100\%$$

Alternatively, the Lorentzian component of a CW peak shape has the expression

$\gamma = (X + X_e \cos \phi)/\cos \Theta + (Y + Y_e \cos \phi) \tan \Theta$

and the strain term is the one that varies with $\tan \Theta$. Again any instrumental or spectral contribution can be subtracted to yield the strain component. This is in centideg and is already a full width at half maximum so the strain is

$$S = \frac{\pi}{18000}(Y - Y_i)\ 100\%$$

As in the case of TOF data the parallel and perpendicular anisotropic strain components can be calculated by

$$S_{|} = \frac{\pi}{18000}(Y + Y_e - Y_i) 100\%$$

$$S_{\perp} = \frac{\pi}{18000}(Y - Y_i) 100\%$$

Particle size broadening

For the case of a CW experiment the particle size broadening can be obtained from

$$\Delta d/d^2 = \frac{\Delta 2\Theta \cot \Theta}{d} = \text{constant}$$

From Bragg's law then

$$\Delta d/d^2 = \frac{2\Delta 2\Theta \cot\Theta \sin\Theta}{\lambda}$$

The broadening is

$$\Delta 2\Theta = \frac{\lambda \Delta d/d}{2\cos\Theta}$$

The first term in the expression for the Lorentzian broadening is of this form where

$$X = \frac{\Delta d}{d^2}$$

The particle size can be obtained by rearrangement of this expression and converting from centideg to radians by

$$p = \frac{18000K\lambda}{\pi X}$$

where K is the Scherrer constant. The units are Å. The anisotropic particle size components are given by

$$p_{\|} = \frac{18000K\lambda}{\pi(X + X_e)}$$

$$p_{\perp} = \frac{18000K\lambda}{\pi X}$$

In a similar way to the TOF functions #2 and #3, the average stacking fault separation can be obtained from the coefficient X_s by

$$p_s = \frac{18000\lambda}{\pi X_s}$$

The corresponding term in the Gaussian expression is the fourth one. Converting from centideg to radians gives the expression

$$p = \frac{18000K\lambda}{\pi\sqrt{8 \mathit{ln}\, 2P}}$$

and again the units are Å.

Reflection Peak Widths

The reflection peaks are considered to have a definite cutoff at the wings where the magnitude of the function falls below some value. The cutoff positions depend on the nature of the profile function and its coefficients; they are found using numerical techniques by subroutine **PROWDT**; editing of the cutoff factors is done by **EDTPRF**. When a new function is installed, the subroutine **PRCALC** must be modified to call the new routine that generates the function and its derivatives.

Least Squares Theory

The refinement technique used by **GSAS** is the method of least squares and is performed by the program **GENLES**. In general the expressions for the calculated values corresponding to the set of crystallographic observations are transcendental and thus the least squares minimization function is nonlinear and the process is iterative.

For single crystal data the function usually minimized in **GSAS** is

$$M = \sum w(F_o^2 - SF_c^2)^2$$

where S is the scale factor for that data set (or histogram) and the sum is over the entire reflection set. The observed structure factors, F_o^2, are obtained by correction of the raw intensity scans for Lorentz-polarization effects and absorption in the **GSAS** routines **SCABS** and **SCMERGE** as well as background subtraction. The weights, w, are derived from an error propagation scheme during this process and are assumed to be uncorrelated. As indicators of the quality of the refinement a set of residuals are defined as

$$R = \frac{\sum |F_o^2 - SF_c^2|}{\sum |F_o^2|}$$

and

$$R_w = \sqrt{\frac{M}{\sum w|F_o^2|}}$$

The reduced χ^2 or "goodness of fit" is defined by the minimization function as

$$\chi^2 = \frac{M}{(N_{obs} - N_{var})}$$

Alternatively and perhaps better, the function

$$M = \sum w(F_o - SF_c)^2$$

can be minimized. In this case the residuals become

$$R = \frac{\sum |F_o - SF_c|}{\sum |F_o|}$$

and

$$R_w = \sqrt{\frac{M}{\sum w|F_o|}}$$

The χ^2 is defined as above.

In analogy to the single crystal case, the least squares program **GENLES** minimizes for powder data the function (Rietveld, J. Appl. Cryst. 2, 65-71, 1969)

$$M = \sum w(I_o - I_c)^2$$

The quality of least squares refinement in this case is also indicated by some residual functions. These cover different parts of the pattern; one is for just that part of the pattern used in the refinement (marked "FITTED") and the other covers the entire pattern except excluded regions (marked "ALL"). Normally the entire pattern is included in the calculation so these values are the same. Optionally, the regions which have no contribution from Bragg peaks can be excluded from the first calculation. In analogy to the single crystal case, the residuals are defined as:

$$R_p = \frac{\Sigma|I_o - I_c|}{\Sigma I_o}$$

and

$$R_{wp} = \sqrt{\frac{M}{\sum w I_o^2}}$$

The reduced χ^2 is also defined the same way as in the single crystal case by

$$\chi^2 = \frac{M}{N_{obs} - N_{var}}$$

One can hand calculate an "expected R_{wp}" from

$$\text{expected } R_{wp} = \frac{R_{wp}}{\sqrt{\chi^2}}$$

A statistical measure of the serial correlation in the powder pattern differences ($\Delta = I_o - I_c$) as given by Durbin and Watson (Biometrica 58,1, 1971; Hill and Flack, J. Appl. Cryst. 20, 356-361, 1987) is also calculated from

$$D_{dw} = \frac{\sum_{i=2}^{N} (\Delta_i/\sigma_i - \Delta_{i-1}/\sigma_{i-1})^2}{\sum_{i=1}^{N} (\Delta_i/\sigma_i)^2}$$

If no serial correlation is present in the differences then D_{dw} is close to 2. The value at the beginning of a refinement is usually very close to zero because of the strong correlations and it increases to some maximum value as the refinement improves. Normally the correlations are such that a string of differences tend to have the same sign so that D_{dw} will be less than 2 in the final refinement. This indicates that some aspect of the profile model is inadequate and a systematic error remains in the analysis. Depending on the nature of the systematic error, the deviations of the refined parameters from the "true" values may be more is than indicated by the estimated standard deviations given by **GENLES**. Experience has shown that the principal systematic errors in most Rietveld refinements are in the profile functions and that they have little effect on the structural parameters resulting from the least squares analysis.

In **GSAS** it is also possible to provide as a set of observations the expected values for a set of interatomic distances assigning to each an appropriate standard deviation. These so called "soft constraints" are then used to generate a minimization function

$$M = K\sum w(d_o^2 - d_c^2)^2$$

The scaling factor K is used to adjust the contribution of these observations to the total minimization function. Usually K is set large in the beginning of a refinement and progressively made smaller as the model improves. This procedure is used to avoid an inadvertent bias in the results because of an incorrect preconceived notion about the value of the interatomic distances. The large contribution in the beginning of the analysis is used to avoid diverging refinements. These calculations are done in **GENLES** by **BNDCALC** and the editing is by routine **EDTSOFT**.

To minimize M by least squares, a set of derivatives of the function (F_c^2, I_c or d_c^2) with respect to a set of variables is obtained for each data point. These variables comprise a reduced set of parameters (atomic coordinates, thermal parameters, scales, powder parameters, etc.) obtained by successive application of three rectangular constraint matrices.

$$\frac{\partial F}{\partial v_i} = R_{il}U_{lk}S_{kj}\frac{\partial F}{\partial p_j}$$

These matrices are obtained from the rigid body constraints (R_{il}), the user constraints (U_{lk}) and the symmetry constraints (S_{kj}). The symmetry constraints are those required by the crystallographic point group for each atom position and affect the coordinates and anisotropic thermal parameters. The user constraints are those imposed on otherwise unrelated parameters because of some known or presumed relationship. The rigid body constraints are derived from a geometric description of molecular units where the least squares variables are distances, molecular origin coordinates and orientation angles.

This vector of derivatives is then used to produce the least squares normal equations which in matrix form are

$$\sum_{h=1}^{N_s} w_h(F^2_{ho} - SF^2_{hc})\frac{\partial F_{hc}}{\partial v_i} + \sum_{k=1}^{N_p} w_k(I_{ko} - I_{kc})\frac{\partial I_{kc}}{\partial v_i} + \sum_{i=1}^{N_d} w_i(d^2_{io} - d^2_{ic})\frac{\partial d_{ic}}{\partial v_i} = 0$$

where the sums are over the three types of observations. After expansion as a Taylor series and ignoring the high order terms, the set of observational equations becomes

$$\mathbf{Ax = y}$$

where in the case of single crystal data

$$y_i = \sum_{h=1}^{N} w_h \Delta F^2_h \frac{|\partial F^2_{ch}|}{\partial v_i}$$

$$x_i = \Delta v_i$$

$$a_{ij} = \sum_{h=1}^{N} w_h \frac{\Delta|SF^2{}_{ch}|}{\Delta v_i} \frac{\Delta|SF^2{}_{ch}|}{\Delta v_j}$$

There are similar expressions for powder profile intensities and soft constraints on bond lengths. These equations are linear in the Δv_i and can be solved by inverting the symmetric matrix **A** by

$$\mathbf{A^{-1}Ax = A^{-1}y}$$

$$\mathbf{x = A^{-1}y = By}$$

This gives the set of shifts to be applied to the variables. They must be retransformed by the constraint matrices to give the set of shifts to be applied to the parameters

$$\Delta p_j = \Delta v_i R_{il} U_{lk} S_{kj}$$

In **GENLES** the matrix **A** is normalized before inversion by dividing each element by the square root of the product of corresponding row and column diagonal elements.

$$A'_{ij} = \frac{A_{ij}}{\sqrt{A_{ii}A_{jj}}}$$

The same is also done to the vector **y**

$$y'_i = \frac{y_i}{\sqrt{A_{ii}}}$$

This eliminates much of the difficulty of inverting a matrix with as much as 16 orders of magnitude range in the element values and gives a more robust refinement. The inverse matrix **B** and shift vector **x** are recovered by a similar transformation

$$B_{ij} = \frac{B'_{ij}}{\sqrt{A_{ii}A_{jj}}}$$

$$x_i = \frac{x'_i}{\sqrt{A_{ii}}}$$

The inverse matrix B is then used to obtain the variance-covariance matrix by normalizing by the reduced χ^2 .

$$\sigma^2{}_{ij} = \frac{B_{ij}}{\chi^2}$$

The square roots of the diagonal elements of this matrix are then the estimated standard deviations in the shifts that are applied to the least squares variables. It is then assumed that these esd's apply to the variables themselves and proper error propagation through the constraint matrices is used to obtain the esd's for the set of parameters.

These calculations in **GENLES** are performed by **MATSLV** and a set of subroutines called by it for matrix normalization (**MATSCL**), inversion (**LSSS** and **MATINV**) and renormalization (**MATUSCL**).

File Structures in GSAS

Introduction

In this section of the **GSAS TECHNICAL MANUAL** we describe the structures of each type of file generated by the system.

File Name Conventions

All files generated by **GSAS** in the course of calculations on a given structural problem have the same main file name; they differ only in the extension. This file name is chosen by the user with the **'EXPNAM'** option of the main **GSAS** command procedure. This name must be given by the user before beginning work on that problem with **GSAS**. All files are generated in the same directory as the first one and must always reside in a single directory.

EXPNAM.EXP - The Experiment File

Usually the first file produced by the system is the main data and control file, EXPNAM.EXP. On VMS systems, this file is a formatted ISAM (Indexed Sequential Access Method) file. Each record in this ISAM file is 80 characters or less long and starts with a 12 character key which is used by the system to fetch that record from the file; the information on that record is read in fixed format. For the UNIX versions of GSAS, the ISAM structure is simulated by routines within GSAS; the file itself is in direct access format. What follows is an essentially complete listing of all currently defined records in this file with an explanation of each, its format and the source of that record. The records are in alphabetical order by key (blank, upper case and numbers; no lower case or special characters are used for these keys by **GSAS**).

Overall data records

The initial section of records covers overall data for the entire experiment.

```
('       DESCR ',2X,A66)DESCR
```

Main descriptive title for the experiment (66 characters maximum). Entered into the file by **NEWEXP** immediately after creation by **OPNEXP** and edited by **EDTTITL**.

```
('      VERSION',I5)IVERSN
```

Version number for **GSAS**. This is the main flag used to determine whether any of the records in the experiment file have to be modified because of changes in **GSAS**. If the value of IVERSN on the record does not match the current version number then the subroutine **UPDATE1** is called to make the necessary changes. This check is done in subroutine **OPNEXP**, and is done by all programs in **GSAS** that open this file with READ/WRITE access.

```
('    HSTRYnnn',1X,67A)TEXT
          nnn=version number for experiment file
```

History record for **GSAS**; a new one is written as each version of the experiment file is produced and by programs that modify the contents of the file. The TEXT includes the name of the **GSAS** program that produced the file, its version number, and the date and time the file was accessed by that program. Usually listed is some brief indication of what was done by that program; for example, **EXPEDT** lists the major menu requests and **GENLES** gives an indication of the refinement progress. Programs that only read information from the experiment file do not produce a new version or write history records.

```
('  DSGL CDATc',2X,A)CDATA
            c = 1 to 9(max)
```

Distance and angle program controls. The controls are written as a free format string. They are defined and modified by **EDTDIST**. There is one of these cards for each phase, 'c'. The data are flags controlling distance and angle calculation limits and inclusion of data from a peak search of Fourier maps.

```
('  FNDP CDATc',2I5) NPEAKS,MININT
('  FNDP HDATc',15A4) (LHST(I),I=1,M)
           c = 1 to 9(max)
```

Control data for **FINDPK**, the peak search routine for data from the SCD instrument at LANSCE. The first record gives the maximum number of peaks to accept from a histogram and the minimum peak value to use. The second gives the list of histograms to be searched. The first item in the list can be either of the strings, "REST" or "ALL", or a number.

```
('  FOUR CDATc',2X,2A5,A2,A5,A8)(FDATA(I),I=1,5)
            c = 1 to 9(max)
```

Fourier map controls; each control is read as a character string and indicates the type of map, section direction, phase number, print control and a special d_{min} if such is needed. One of these records is written by **EDTFOUR** for each type of map to be calculated. Fourier map control data for only one phase can be generated at a time. They are read by **FOURIER** to set up map calculations.

```
('  GNLS  RUN ',A43,I4,G17.5)TEXT,NCYCLES,CHISQ
```

Least squares run indicator; it gives the date, time and total number of cycles attempted for the experiment and the latest value of χ^2. This is used by **POWPLOT** to produce the secondary plot title and by **DISAGL** to coordinate the variance-covariance matrix with the structural parameters.

```
('  GNLS CDATc',2X,8A8)(CDATA(I),I=1,M)
            c = 1 to 9(max)
```

Least squares controls (maximum number of cycles, etc.). Each control is an 8 character string and is entered by **EDTLSQ**. There may be more than one of these records. The controls are read for **GENLES** by **RDLSCNTL**.

The next few records contain the control data for **INTEGRATE**, the program for extracting intensity data from the LANSCE single crystal instrument, SCD. They are edited by **EDTINGRT**. They are read in the integration program by **INGREAD**.

```
('  INGT CDAT1',2F5.3,F6.3)WNDOX,WNDOZ,EMIN
```

These parameters define the *x*,*y* dimensions of the reflections for integration. The first two values define the spot size and the region to used for background evaluation. The last item, EMIN, is used for a minimum count cutoff to limit the region of integration.

```
('  INGT CDAT2',2F6.1,12X,2F6.3)SG0,SG1,BE0,BE1
```

These data define the shape of the peak along the time direction. They are quite similar to those used in the powder profile parameters.

```
('  INGT CDAT3',2F5.2,7F4.1,F6.3,1X,A,2I3)BINMIN,VRATMX,(RAT(I),I=1,7),
                                            DMIN,SOLLER,IXL,IXU
```

Integration limiting and final data selection flags. BINMIN defines the minimum fraction of a peak included in the integration for accepting the value. VRATMX determines the maximum ratio peak to background allowable for the peak to be included. This can get very large if the peaks are very dense. The seven RAT values are I/sig(I) cutoffs used for creating a table of data with which the quality of the data can be evaluated. SOLLER and IXL and IXU define the Soller shield used on SCD from 1982 until mid 1988.

```
('  INGT HDATc',15A4) (LHST(I),I=1,M)
            c = 1 to 9(max)
```

The list of histograms for integration. Histograms can be summed together before integration of the reflection data. This is accomplished by entering -h for histograms which are to be added to the current data before integrating.

```
(' AFAC aaaa  ',9F7.0)(FFAC(I),I=1,9)
           a = element symbol
```

The first atom data record for atom type 'a'. The element symbol consists of the standard two letter chemical symbol (upper case) and the valence as a sign and a numerical value, e.g. 'TI+4'; this is part of the key. The 9 values are the coefficients for the x-ray scattering factor for that chemical species as listed by Cromer & Waber (1974), International Tables for X-ray Crystallography, Vol. IV, p 99-101. This and the succeeding 'AFAC' cards are copied from the atom data file by **REDSCTF** whenever a new atom TYPE is input by the user into **EXPEDT**. These records are read by **RDSCFT** in **GENLES**.

```
(' AFAC aaaa M',9F7.0)(MFFAC(I),I=1,9)
           a = element symbol
```

This record is the exception to the rule just noted. It is present only when a magnetic form factor has been entered into the experiment in **EXPEDT** using the form factor editing option in the 'Least Squares' editing menu and magnetic form factors are selected. The data for this record is not currently in the atom data file to be described later. Data in table 4.4.5.1 of International Tables for X-ray Crystallography, Vol. C, can be used as listed for the elements and ions in that table. Data for other atoms or ions can be derived from tables

4.4.5.2-14 of that source. Alternatively, one can read a file containing the scattering factor data as a function of $\sin\theta/\lambda$ and fit it to the needed function in subroutine **EDTMFF**.

```
(' AFAC aa_nnn',F7.0,4F6.0)WT,BLEN,RNMU,RNMUX
```

The isotopic data for 'aa_nnn' where 'aa' is the chemical symbol (upper case) and 'nnn' is the isotope. The data are isotopic weight, real neutron scattering length, and the wavelength dependent and wavelength independent neutron absorption cross sections. Since there are only a very few atomic isotopes for which an imaginary scattering length is needed, we do not currently have that data in our data base. If 'nnn' is blank then the data are for the natural abundance element. Synthetic elements do not have 'natural abundance' data.

```
(' AFAC aa_SIZ',2F10.2,F5.2,I5)DRAD,ARAD,PRAD,COLOR
```

This record contains default atom size data for distance/angle calculations and for the structure plotting programs.

```
(' AFAC aa_XAB',1X,5F6.0)(RXMU(I),I=1,5)
```

The x-ray absorption cross sections for Cr, Fe, Cu, Mo and Ag Kα radiation.

```
(' AFAC aa_XAN',1X,10F6.0)(XFP(I),XFPP(I),I=1,5)
```

The real and imaginary parts of the anomalous dispersion for Cr, Fe, Cu, Mo and Ag radiation for the a-th atom type.

```
(' EXPR  HTYPc',2X,12(A4,1X))(HTYP(I),I=1,NHST)
              c = 1 to 9(max)
```

The histogram type flags, HTYP, are 4 character strings which indicate the type of sample (P: powder or S: single crystal), type of radiation (N: neutron or X: x-rays), type of data (T: time of flight or C: constant wavelength) and the status of the data set (blank: use in least squares, D: dummy powder histogram not processed by **GENLES**, F: SCD histogram peak positions have been determined by **FINDPK**, G: SCD histogram peak positions found by **FINDPK** but will not be used, I: SCD histogram intensity data generated by **INTEGRATE**, N: new SCD histogram not yet processed by **FINDPK**, R: read powder histogram, X: powder profile not processed by **POWPREF** or *: do not use in least squares). Thus the flag 'PNT ' means that this histogram is neutron TOF powder data that can be used in a least squares refinement. The special histogram type 'RSN ' is used for "soft" constraints which are treated as a set of observations and are placed in their own histogram. There is one type for each histogram and they are in the order of the histogram numbers. These flags are generated in several places in **GSAS**, and the records are written by **WRHTYP** and read by **RDHTYP**.

```
(' EXPR  NATYP',I5)NATYP
```

The number of atom types. The maximum number of atom types is 9 due to limitations imposed by array sizes in **GENLES** and **EXPEDT**. This value is updated by **TYPINS** and **TYPDEL**. This value is read by **RDSCFT** in preparation for reading the scattering factors.

```
(' EXPR  NHST ',I5)NHST
```

The number of histograms, **NHST**, loaded into the **GSAS** system for this problem. This value never decreases and is updated when new histograms are read by **HSTINS** for powder data, **REDHST** for SCD single crystal data, **CAD4RD** for Enraf-Nonius CAD4 data and generated by **EDTSOFT** for soft constraint data.

```
(' EXPR ATYPnn',2X,A8,I5,2F10.0,F5.2,I5)TYPE,NATOM,DRAD,ARAD,PRAD,COLOR
             n = 1,NATYP
```

Record contains the atom type, the number of atoms of that type in all phases and atom radii limits for distance and angle calculations and data for structure plotting. The type matches that used for an individual atom entry (see below) and is composed of the chemical symbol (upper case) valence (if any) and isotope (if any). The form of the type is 'aasv_nnn' where 'aa' is the chemical symbol, 's' is the valence sign (+ or -), 'v' is the valence (typically 1-6) and 'nnn' is the isotope number. The number of atoms is incremented when a new atom of that type is added and decremented when an atom is deleted. If this value reaches zero then this record is deleted, however the 'AFAC' records for this atom type are not deleted. The atom radii are edited by **EDTDIST** and read by **DISAGL**.

```
(' EXPR ftypRL',I10) LENREC
```

This record is written by **FOURPRT4** within **FOURIER** and contains the length of records in the 'ftyp' Fourier map file. 'ftyp' is one of 'FOBS', 'FCAL', DELF', PTSN', or 'DPTN'. It is read by the Fourier map processing or plotting routines in preparation for opening the appropriate map file.

```
(' EXPR NMXTLS',9I5)(NMXTLS(IPHAS),IPHAS=1,9)
```

This record is written by **INDEXSCD** and records the number of separate crystals found for each phase in a single crystal experiment. These crystals may be multiple crystals in a histogram, or they may be separate settings of a single crystal which fell off in the middle of an experiment, or separate crystals used because of crystal loss, etc. The code allows for up to nine crystals per phase. The record is read in several places in the processing of single crystal data from the SCD instrument.

```
(' EXPR NPHAS ',9I5)(NPHAS(IPHAS),IPHAS=1,9)
```

Phase flags for phase number IPHAS. The value of each flag is 1 if there is just nuclear phase information, 2 for mixed nuclear and magnetic phase information, 3 for magnetic only phase information, or zero if the phase is absent. This record is updated by **EDTPHAS** and is read in many places in **GSAS**.

Crystal structure records

The next section of records are specific structural information for each phase, p, in the sample.

```
('CRSp    PNAM',2X,A66)PNAM
```

A characteristic name for the phase; entered by the user in **EDTPHAS** and used for various heading titles.

```
('CRSp   ABSCO',7F10.2)(XAB(I),I=1,5),RNMU,RNMUX
```

Computed absorption coefficients for this phase based on the chemical formula and the five x-ray wavelengths and the two neutron absorption coefficients. This and the next three records are changed by **EDTCOMP** any time the chemical formula is changed.

```
('CRSp   ATYPS',I5)NATYPS
```

Number of atom types for this phase; used to read the formula record, `'CRSp   FRMLc'`, shown below.

```
('CRSp   F000 ',2F10.0)FNEUT,FXRAY
```

The F_{000} scattering factors for neutrons and x-rays based on the chemical formula.

```
('CRSp   FRMLc',4(2X,A8,F6.2)(ATYP(I),NAT(I),I=1,NATYPS)
             c = 1 to 1+(NATYPS-1)/4
```

The contents of the unit cell for this phase. Used to calculate absorption coefficients, formula weight, density and F_{000} values.

```
('CRSp   NATOM',I5)NATOM
```

The number of atom positions for this phase. This record is updated by **ATMINS** and **ATMDEL**; if it reaches zero the phase can be deleted by **PHASDEL**.

```
('CRSp  ABC   ',3F10.6,4X,A1,4X,I1)(ABC(I),I=1,3),IREF,IDAMP
('CRSp  ABCSIG',3F10.6)ABCSIG(I),I=1,3
('CRSp  ANGLES',3F10.4)ANGLES(I),I=1,3
('CRSp  ANGSIG',3F10.4)ANGSIG(I),I=1,3
```

The first record contains the real lattice edge lengths for the phase, a refinement flag and a damping factor. The third contains the lattice angles. If the refinement flag is 'Y' then the lattice parameters (as reciprocal metric tensor elements) will be refined. Refinement is possible with powder diffraction data and single crystal data from SCD type instruments. The damping defines what fraction of the calculated shift is applied to give the new values of the parameters. The applied shift is (10-IDAMP)/10 times the calculated shift. The second and last records are the estimated standard deviations in the lattice parameters.

```
('CRSp  ATmmmA',2X,A8,4F10.6,A8,I4,1X,3A1) ATYP,X,Y,Z,FRAC,
                         NAME,MULT,(IDAMP(I),I=1,3)
('CRSp  ATmmmB',6F10.6,2X,4A1) (UIJ(I),I=1,6),(CODE(I),I=1,4)
      m = 1 to NATOM
```

Atom parameter records for atom 'm'; the first one contains the atom type (matches one of the atom types given above), fractional coordinates, atom fraction, atom name (chosen by user), multiplicity of atom site, damping factors for FRAC, XYZ and UIJ. The second contains the temperature factors; if CODE(1) = 'I' then UIJ(1) is U_{iso}, if CODE(1) = 'A' then six anisotropic u_{ij} values are given. If CODE(2) = 'F' then FRAC is to be refined; if CODE(3) = 'X' then XYZ's are to be refined as permitted by symmetry; and if CODE(4) = 'U' then U_{iso} or the u_{ij}'s are to be refined as permitted by symmetry. These records are written by **WRTATM** and read by **REDATM**; the parameters are edited by several atom editing routines called from **EDTATM**.

```
('CRSp  ATmmmM',3F10.5,2(1X,A2),3F10.3) (ATMON(I),I=1,3),
                        CODE(5),IDAMP(4),(ATMON(I),I=4,6)
      m = 1 to NATOM
```

The magnetic moment data record for atom 'm', ATMON(1-3) give the components of the magnetic moment along the three orthogonal directions defined earlier, ATMON(4-6) are the magnitude of the moment and the moment orientation angles, ψ and ω relative to the orthogonal Z- and X-axes. CODE(5) = 'M' to refine the moment and IDAMP(4) is the damping factor to be applied as defined above.

```
('CRSp  CELVOL',2F10.3)CELVOL,SIGCVL
```

The unit cell volume and esd; this record is updated each time the lattice parameters are changed.

```
('CRSp  DENSTY',F10.3)DENSTY
```

The density of this phase in Mg/m^3; this record is updated by **EDTCOMP** any time the chemical formula is changed. It is not affected by atom parameter refinement or atom editing.

```
('CRSp  FMHSTn',20I3)HSTLST
             n = 1 to 9 (max)
```

The list of included histogram numbers to use for the Fourier calculation. The structure factors are read from the histograms in the order as shown. The last occurrence of a structure factor is the one used in the calculation. Mixing of x-ray and neutron histograms is not allowed. This record is written by **EDTFOUR** and read by **FOURIER** when the map is calculated.

```
('CRSp  FMPCTL',9I5)NXI,NYI,NZI,NXO,NYO,NZO,NXT,NYT,NZT
```

This record gives the number of steps along the cell edges, the starting step position and the ending step position for a Fourier map calculation. It is written by **EDTFOUR** and read by **FOURIER** when the map is calculated. This information is then written in the second record of the Fourier map file during processing by **FOURIER** (see below).

```
('CRSp  FPK   ',2X,A66)TEXT
```

This record gives the time and date of extraction of peak positions from a Fourier map along with the map type that was processed by **FORSRH**. It is written by **FRSHR**.

```
('CRSp  FPKnnn',3F10.5,F10.3)(XN(I),I=1,3),IXN
```

These records contain the positions and heights of the peaks extracted from a Fourier map. They are written by **FRSHR** and can be read by **DSGREAD** for distance and angle calculations by **DISAGL** and **FPLTATM** for plotting on contoured maps produced by **FORPLOT**

```
('CRSp  MRG-R ',4(A,F6.3),A,I5)' wR(Fsq)=',R1,' wR(F)=',R2,
                        ' R(Fsq)=',R3,' R(F)=',R4,' N(I)=',NREF
```

Record written by **SCMERGE** giving the R-factors from the merge of equivalent reflections and the number of resulting unique reflections.

```
('CRSp  MXDSTR',F10.5) DSTRMX
```

The maximum d^* for magnetic reflections in this phase. This record is produced by **ATMMAG** and used by **CELLINP**.

```
('CRSp  PEAKRD',2F6.0,11F5.2)PKMAX,PKMIN,FDRAD,FARAD,
                              (REJRAD(I),I=1,NATYP+1)
```

Distance and angle code controls for processing peak information from **FORSRH**. The data are peak minimum and maximum values, the radius of the peak for distances and angles, and the peak overlap rejection radius for each atom type and for the peaks themselves. This record is produced by **EDTDIST**.

```
('CRSp  SG SYM',2X,A20)SPSGSYM
```

The space group symbol for this phase. The symbol is entered by the user to **SPSGSYM** which calls the space group interpreting routine **SGROUP** before entering it into the file. This record is read in other parts of **GSAS** which then call **SGROUP** to produce all the relevant symmetry information.

```
('CRSp  SPAXIS',3F5.0,4x,A,6F5.0)PAXIS,NAXIS,UAXIS,VAXIS
```

The principal broadening axis, PAXIS, for this phase; it is used to calculate the anisotropic broadening terms in some of the powder profile functions. If NAXIS is 'Y' then two additional axes are defined for the sublattice of reflections that are subject to a different anisotropic particle size broadening than the nonsublattice reflections. This facility is used by some of the profile functions to simulate broadening due to stacking faults. This record is edited by **EDTPRF**, and input by **PRFCINP** and output by **PRFCOUT**.

```
('CRSp  SPNFLP',12F4.0)(SPNFLP(I),I=1,12)
```

This record contains the current state of the spin flip operations to create the magnetic space group from the nuclear one for this phase. The values are +1.0 for no spin flip and -1.0 for spin flip. This record is created by **ATMMAG** and read by **POWPREF** and **ATMSINP**.

```
('CRSp  UCRFLn',20I3)(IPARM(I),I=1,60)
             n=1,3
```

Refinement flags used in **CELLLSQ**. This record will only appear while processing LANSCE SCD data.

```
('CRSpe EXTSN ',I5,2X,3A,2X,3I1)EXTTYP,IEXCOD,(IDAMP(I),I=1,3)
('CRSpe EXTSN1',3E10.3)(EXTSING(I),I=1,2),EXTRPRI
```

Single crystal extinction flags and coefficients. They are edited by **EDTEXTS**, input by **EXTSINP** and output by **EXTSOUT**. There is a set for each phase and crystal element in the sample.

```
('CRSpe HKLDnn',4F10.4)
```

These records describe the crystal shape for use in absorption calculations in **SCABS**. They are written and edited by **EDTPLNS**.

```
('CRSpe O-CHI ',2F10.3) CHI,SIGCHI
('CRSpe O-OMG ',2F10.3) OMG,SIGOMG
('CRSpe O-PHI ',2F10.3) PHI,SIGPHI
```

Single crystal element orientation angles. The three orientation angles required to position the 100 reciprocal lattice vector into the reflecting position with the *hk0* set of vectors in the standard xy plane on a single crystal goniometer. The ω angle is measured away from the y-axis, χ from the negative z-axis and ϕ is arbitrary. These records are initially written by **INDEXSCD** and later are modified by **CELLLSQ** which adds the sigmas.

```
('CRSpe PTYPE ',2X,A8,I4,F8.2)PTYPE,NPLANES,PHI0
```

The record describes the way that the faces of a faceted crystal are defined. The data are PTYPE, a flag defining the face definition, NPLANES, the number of faces, and PHI0, the ϕ angle at which the diffractometer *x*-axis and the crystal *x*-axis are coincident if PTYPE='3 POINTS' and θ,χ and ω are zero. This record is written by **EDTPLNS** and is read by **PLANIN** in the single crystal absorption program **SCABS**.

```
('CRSpe XD0   ',3F10.2) (XD0(I),I=1,3)
('CRSpe XD0SIG',3F10.2) (SIGXD0(i),I=1,3)
```

Crystal miss-centering vector and its estimated standard deviation. These records are initially written by **INDEXSCD** and modified by **CELLLSQ**. This data is used by all codes which need to calculate detector coordinates for reflections from reflection indices or to calculate reflection indices from detector locations.

Histogram/phase records

The next section of records contains information that depends on both the histogram, h, and crystalline phase, p; hence the key prefix 'HAP'.

```
('HAPphh ZONE',4I5)ZONE
```

The first three coefficients describe the zone axis restricting the reflection set for a powder pattern. The fourth coefficient is the layer number. If all zeros there is no restriction on the reflection set. This record is written by **EDTZONE** and read by **REFGEN** in **POWPREF**.

```
('HAPphhELMFRn',G16.4,4X,A,I5)SCALE,REFCOD,DAMP
```

Crystal element fraction for this phase and histogram combination, refinement flag and damping flag. This is used for a single crystal histogram. Editing is done by **EDTSCAL**, least squares input by **SCALINP** and output by **SCALOUT**.

```
('HAPphhEXTMAX',A,F8.5)TEXT,EXTMAX
```

This record gives the maximum extinction correction applied to any reflection in this phase and histogram. It is written by **SNGLXTL** in **GENLES** as each histogram is processed.

```
('HAPphhEXTPOW',E15.6,4X,A1,4X,I1)EXTPOW,IREF,IDAMP
```

The powder extinction coefficient, its refinement flag and damping factor. These are edited by **EDTEXTP**, input by **EXTPINP** and output by **EXTPOUT**.

```
('HAPphhNAXIS ',I5)NAXIS
```

This gives the number of preferred orientation axes in the March-Dollase model used for powder diffraction data. It determines the number of `'HAPphhPREFOn'` (see below) records are read for this phase/histogram combination. It is created by **EDTPRFO** and used by **PRFOINP**.

```
('HAPphhPHSFR ',G15.6,4X,A1,4X,I1)SCALE,IREF,IDAMP
```

Phase fraction for this phase and histogram combination, refinement flag and damping flag. This is used for a powder diffraction histogram. Editing is done by **EDTSCAL**, least squares input by **SCALINP** and output by **SCALOUT**.

```
('HAPphhPRCF  ',2I5,F10.5,4X,I1,20A1)
                   PTYP,NCOF,CTOF,IDAMP,(IREF(I),I=1,NCOF)
('HAPphhPRCF c',4E15.6)(COF(I),I=1,NCOF)
              c = 1 to 1+(NCOF-1)/4
```

The first record contains the powder profile type, number of coefficients, cutoff factor, damping flag and a refinement flag for each coefficient. The second and subsequent record (c = 1,...) contain the coefficients with four per record. These are edited by **EDTPRF** and routines called by it, input by **PRFCINP** and output by **PRFCOUT**.

```
('HAPphhPREFOn',4F10.5,4X,A1,2I5)PRFCOF,(PHKL(I),I=1,3),REFCOD,DAMP,TYPE
              n=1,NAXIS
```

This record gives the preferred orientation coefficient, direction, refinement code, damping factor for preferred orientation axis 'n', and preferred orientation function type. The number of these records is determined from the `'HAPphhNAXIS '` (see above). These are edited by **EDTPRFO**, input by **PRFOINP** and output by **PRFOOUT**.

```
('HAPphhXTLELM',2X,9I2) (XTLELM(IPHAS,IELEM)
```

This record notes which crystal elements of phase, IPHAS, are present in this histogram. The record is written by **INDEXSCD** and read by all programs needing to process reflection data, such as **INDEXSCD**, **CELLLSQ**, and **INTEGRATE**. A dummy record with XTLELM(1,1)=1 is entered for powder histograms.

Histogram records

The next section of records contains only histogram specific information. This section is described in four parts each covering the records that are specific to particular types of histograms

All diffraction histogram types

The following records are found in the experiment file for all diffraction histogram types. Some of these are not needed for histograms from TOF neutron single crystal diffractometers (SCD instruments); they will be so indicated

```
('HST hh  HFIL',2X,A66)RAWNAM
```

The file name of the **GSAS** standard powder data file or SCD raw data file which is the source of this histogram. This name uses whatever logical names the user had in force to describe this file at the time the file was introduced to experiment by **EXPEDT** for powder data, by **REDHST** for SCD data, or by **CAD4RD** for single crystal x-ray data.

```
('HST hh  HNAM',2X,A66)HNAM
```

A histogram title taken from the title record on the **GSAS** standard powder data file or from the cataloging string for SCD data.

```
('HST hh  IFIL',2X,A66)INSTNAM
```

The file name of the instrument parameter file associated with this histogram. This file name also uses logical names.

```
('HST hh IRAD ',I5)IRAD
```

This is an integer (1 to 5) indicating which characteristic radiation (Cr, Fe, Cu, Mo or Ag Kα, respectively) was used for the data collection. This record originates from the instrument parameter file and is read by **PDCALC** or **SNGLXTL** as the histogram is processed. It is only needed for x-ray data. If IRAD is zero the wavelength is not one of the five standard ones and special anomalous dispersion data is needed for the histogram; these are the FFANS records described below.

```
('HST hh NREF ',I5,F10.4,4X,A1)NREF,DMIN,IFFOS
```

The number of reflections in the 'EXPNAM'.REFPhh or the 'EXPNAM'.REFShh reflection file, the minimum d-spacing and a flag for powder data indicating whether F_o^2's have been extracted from this histogram. This record is produced when the reflections are generated by **REFGEN** for powder data and by the several routines that process single crystal data. The flag is set by **PDCALC** to 'Y' after it has produced F_o^2's and places them in the reflection file.

```
('HST hhFFANSc',2X,A8,2F10.3,3X,2A1,I5)ATYP,DELFP,DELFPP,IRE,DAMP
             c = 1,NATYP
```

The special anomalous dispersion coefficients for x-ray data with a non-standard wavelength. Included is two refinement flags and a damping factor. These records are required when IRAD is zero and there must be one for each atom type in the same order as the `' EXPR ATYPnn'` records above. These are edited by **EDTFFAC**, input by **FFACINP** and output by **FFACOUT**.

```
('HST hhOMEGA ',F10.3)OMEGA
('HST hhCHI   ',F10.3)CHI
('HST hhPHI   ',F10.3)PHI
```

These are the sample orientation angles with respect to the diffractometer which are used for generalized texture analysis of polycrystalline samples. They are defined in much the same way as for a single crystal diffractometer (see `'CRSpe O-CHI '`, etc. records above). These records are wirtten by **HSTCHG**.

```
('HST hhREFLEN',I5)REFLEN
```

This record gives the length of the records in the .REFhht files, where 't' is 'M', 'P' or 'S' for single crystal merged data, powder or single crystal data respectively.

Powder histogram records

All of this information which is related to powder histograms is entered into the experiment file by **HSTINS** when the histogram is first read.

```
('HST hh BANK ',I5)IBANK
```

The counter bank number for the diffractometer.

```
('HST hh CHANS',6I10)HOLDOFF,ICLMP,NCHANS,CHEKHST,MCHANS,ISAMP
```

The holdoff for the first channel in the output powder histogram from **POWPREF** (HOLDOFF), the number of original data channels combined in each bin (ICLMP), number of steps in the original profile (NCHANS), a checksum for the intensities (CHEKHST), the number of bins used in the calculations (MCHANS), and the sampling frequency (ISAMP). The checksum is computed from the raw data and is used to check whether a data set has been read previously.

```
('HST hh DUMMY',I10,2X,A,3X,2F10.3)NCHAN,BINTYP,(BCOEF(I),I=1,4)
```

These are the control values needed for dummy powder histogram generation. NCHAN is the number of channels desired, BINTYP is either 'CONST' or 'LOG6' and BCOEF includes the holdoff for the first channel and either the step size or the clock increment.

```
('HST hh EPHAS',9I5) (EPHAS(I),I=1,9)
```

Flags to control the extraction of integrated intensities for the reflections in the histogram. The flags are generated in **EDTEXTFOS** and read in various places in **GENLES**.

```
('HST hh ICONR',3F10.0,2X,3A1,4X,I1,F10.0,I5,F10.0)
                    DIFC,DIFA,ZERO,IREF,IDAMP,POLA,IPOLA,KRATIO
('HST hh ICONS',3F10.0,2X,3A1,4X,I1,F10.0,I5,F10.0)
                    DIFC,DIFA,ZERO,IREF,IDAMP,POLA,IPOLA,KRATIO
```

These are the diffractometer constants for a powder diffractometer. In the case of a TOF diffractometer the constants relate d-spacing and TOF in µsec. For CW data the same record holds wavelength data, LAM1 and LAM2, in place of DIFC and DIFA and KRATIO is added to the record. The polarization coefficient POLA is absent for neutron data. The ICONR record contains the initial values for these coefficients as obtained from the instrument parameter file and is used to reset the values if needed. These are edited by **EDTDIF**, input by **DIFSINP** and output by **DIFSOUT**.

```
('HST hh MAXRF',I5)MAXRF
```

The maximum number of overlapping reflections for any point in the powder pattern. This value is determined by **HSTMACH** in **POWPREF** and is used to determine the size of the arrays that hold reflection information in **PDCALC**.

```
('HST hh NEXC ',I5)NEXC
```

The number of excluded regions in the pattern. There is always at least two; one for the short end of the pattern and one for the long end. These are edited by **EXCLCHG**. The first excluded region record for TOF data and the last one for CW data can be modified only by setting the minimum d-spacing in **ESTDMIN**.

```
('HST hh NFXB ',I5)NFXB
```

The number of fixed background points in this histogram.

```
('HST hh NPHAS',9I5)NPHAS
```

Phase flags for this histogram. The value of each flag is 1 if there is just nuclear phase information, 2 for mixed nuclear and magnetic phase information, 3 for magnetic only phase information, or zero if the phase is absent. This record is updated by **EDTHPHAS** and is read in many places in **GSAS**.

```
('HST hhABSCOR',2E15.6,4X,A1,2I5)ABSCOR(I),I=1,2,IREF,IDAMP,IABTYP
```

The powder absorption coefficients, refinement flag, damping flag, and absorption type flag. These are edited by **EDTABS** and input and output by **ABSCINP** and **ABSCOUT**, respectively.

```
('HST hhBAKGD ',2I5,4X,A1,I5,4X,A1)BTYP,NCOF,IREF,IDAMP,IFULL
('HST hhBAKGDc',4E15.6)(BCOF(I),I=1,NCOF)
               c = 1 to 1+(NCOF-1)/4
```

The first record contains the background function type, the number of coefficients (maximum of 36), refinement flag, damping factor and full background refinement flag. The second and subsequent records contain the coefficients. These are edited by **EDTBAK** and are input and output by **BACKINP** and **BACKOUT**, respectively.

```
('HST hhBNKNAM',A) BNKNAM
```

The name of the data bank used to collect the histogram. This name for TOF instruments usually gives the detector bank location. The record is purely for descriptive purposes.

```
('HST hhBNKPAR',5F10.0,2I5)DIST,TTHETA,TILT,SEPN,HGHT,NTUBE,ITUBE
```

This record describes a TOF detector bank. This data is used by **FSTBUSBIN** to compute the spectrum shift factors required to bin multiple detectors into a single data set when the `'HST hhBNKTCc'` records are absent. The second term, TTHETA (2Θ), is read as part of the preparation of powder plot titles and for powder absorption and extinction calculations. This record originated from the instrument parameter file.

```
('HST hhBNKTCc',8F8.2)(DIFC(I),I=1,NTUBE)
             c = 1 to 1+(NTUBE-1)/8
```

These are the individual DIFC values for each tube in a bank of detectors; these are used by **FSTBUSBIN** to calculate the spectrum shift factors. As with the previous record, these records are copied from the instrument parameters file.

```
('HST hhEXCeee',2F10.3)(EXCM(I),EXCX(I),I=1,NEXC)
             e = 1 to NEXC
```

The excluded regions from EXCM to EXCX in msec or degrees 2Θ; there are at least two of these records. These records are edited by **EXCLCHG** and **ESTDMIN**. The excluded regions are marked in the profile by **HSTPROC**.

```
('HST hhFXB cc',3F10.2)(TOFB(I),BAK(I),SBAK(I),I=1,NFXB)
             c = 1 to NFXB
```

The position, fixed background and estimated error in the fixed background value. If these are present they should include a point at each end of the histogram even if the values are zero at those points. These are edited by **FBAKCHG**.

```
('HST hhHSCALE',G15.6,4X,A1,4X,I1)SCALE,IREF,IDAMP
```

Scale factor for this histogram, refinement flag and damping flag. The net scale factor for a phase in a powder histogram in the product of this scale and the 'HAP' PHSFR listed above. This feature can be used in multiphase mixtures to separate the phase fraction from the histogram scale. Editing is done by **EDTHSCAL**, least squares input by **HSCALINP** and output by **HSCALOUT**.

The next series of five record types characterize the incident spectrum and are copied from the instrument parameter file. The data are defined by the program **FITSPEC**. All of these are read by **HSTPROC** the first time a powder histogram is processed by **POWPREF**.

```
('HST hhI HEAD',2X,A66)IHEAD
```

A title taken from the incident spectrum raw data file.

```
('HST hhI ITYP',I5,2F10.4,I10)ITYP,TMIN,TMAX,CHKSUM
```

The incident intensity function type, the minimum TOF, the maximum TOF over which the function can be applied and a checksum on the incident spectrum. The latter is used to check if this incident data has been applied to another histogram.

```
('HST hh TRNGE',2F10.5)TMIN,TMAX
```

The actual range of data in msec TOF or degrees 2Θ as delimited by the excluded regions. This record is written by **HSTPROC** and is used by **BACKCAL** and **CALCBAK** for computing function #1 (Chebyschev series).

```
('HST hhICOFFc',4E15.6)(VINC(I),I=1,12)
             c = 1 to 3
```

Coefficients for the incident intensity function; they are expressed in terms of TOF in milliseconds. If ITYP above is zero these records are not needed.

```
('HST hhIECOFc',4E15.6)(SINC(I),I=1,12)
             c = 1 to 3
```

The σ's for each of the coefficients. If ITYP above is zero these records are not needed.

```
('HST hhIECORc',10F6.3)(PINC(I),I=1,78)
             c = 1 to 8
```

The elements of the correlation matrix in upper triangular form for the incident intensity coefficients. These with the σ's are used to calculate the σ in the calculated incident intensity at each point in the profile. If ITYP above is zero these records are not needed.

```
('HST hhPRCFn ',2I5,F10.5,4X,I1,20A1)
                  PTYP,NCOF,CTOF,IDAMP,(IREF(I),I=1,NCOF)
            n = 1,NTYP
('HST hhPRCFnc',4E15.6)(COF(I),I=1,NCOF)
             c = 1 to 1+(NCOF-1)/4
```

These records give the NTYP sets of profile functions available for the histogram with their default coefficients. The first record contains the powder profile type, number of coefficients, cutoff factor, damping flag and a refinement flag for each coefficient. The second and subsequent records (c = 1,...) contain the coefficients with four per record. These records are obtained from the instrument parameter file and are copied to the 'HAP' records listed above to initialize the profile coefficients for the specific histogram/phase combination. If the user changes to a different type of profile function, these records are the source of the starting values. The first set defines the default profile function type for this histogram, i.e. PTYP for the first set does not have to be 1.

Single crystal histogram records

The following records appear when the histogram is from a single crystal diffractometer. Some are only needed for x-ray or CW neutron diffraction data. Any records that are specific to TOF instruments are described in the next section.

```
('HST hh  INST',I5)INSTNO
```

Record pointing to the appropriate instrument parameter records.

```
('HST hh CDAT1',2(2X,A),1X,L1,3F6.3)DATASRC,ABSTYPE,PRTREF,
                                      SHPRAD,ERRINS,DSMAX
```

Histogram dependent control data for **SCABS**. DATASRC is the radiation type (i.e. CuKa), ABSTYPE is the absorption correction type, PTREF is a logical controlling the printing of reflections by **SCABS**, SHPRAD is the sphere radius in mm, ERRINS is the instrument error constant and DSMAX is the maximum value of d*. Written by **EDTSCAB** and read by **SCABS**.

```
('HST hh NPSI ',4I5)NPSI,PSIHKL
```

The number of measurements of the ψ-scan reflection and its *hkl* index. This record is written by **PSISCNDTA** in **CAD4RD** and read by **EDTSCAB** and **SCABS** for absorption corrections.

```
('HST hh NREFM',I5,F10.4)NREFM,DMIN
```

Used only for single crystal data collected with constant wave-length methods. This gives the number of reflections in the merged data set generated by **SCMERGE**. The DMIN is carried over from the raw unmerged data set. This is the number of reflections in the "EXPNAM".REFMhh reflection file.

```
('HST hhCOS2TM',F10.5)COS2TM
```

For single crystal x-ray diffractometers equipped with a monochromator, the value of $\cos 2\Theta_m$. It is used to calculate the Lorentz-polarization correction as part of the single crystal extinction calculation.

```
('HST hhFSQMAX',E15.6)FSQMAX
```

This single crystal data record is written by **SCABS** and is used to format the output of reflection data from **REFLIST**.

```
('HST hhLAMBDA',3F10.5)LAMBDA
```

The values of the x-ray or neutron wavelengths for a CW single crystal experiment. It is used in the extinction calculations.

```
('HST hhO-CHI ',F10.3)CHI0
('HST hhO-OMG ',F10.3)OMG0
('HST hhO-PHI ',F10.3)PHI0
```

These three records give the orientation angles for the crystal as mounted on a single crystal goniometer. They are used in **SCABS** to calculate to orientation matrix in preparation for absorption corrections.

```
('HST hhPSIINT',F10.5)PSIINT
```

Interval in degrees for the ψ-scan. Written by **PSISCNDTA** in **CAD4RD** and read by **SCABS**.

```
('HST hhPSIAmn',9F7.4)(PHIANG(I=1,MPSI)
             n = 1 to MPSI/9
```

The ψ-angles at which the ψ-scan data were measured. This data is associated with crystal element 'm'. There usually are 360/PSIINT values in the list, but some points may be missing for various reasons. This data is written by **PSISCNDTA** in **CAD4RD**, can be edited in **EDTSCAB** in **EXPEDT** and is read and used by **SCABS**.

```
('HST hhPSIVmn',9F7.4)(PHICOR(I=1,MPSI)
             n = 1 to MPSI/9
```

The normalized ψ-scan intensities. This data is associated with crystal element 'm'. There are 360/PSIINT values in the list. This data is written by **PSISCNDTA** in **CAD4RD** can be edited in **EDTSCAB** in **EXPEDT** and is read and used by **SCABS**.

```
('HST hhTRNSLM',2E15.6)TRMX,TRMN
```

The maximum and minimum values for the transmission (1/absorption) for this histogram as computed by **SCABS** which writes this record.

SCD instrument histogram records

These records are unique to TOF neutron single crystal diffractometers (SCD instruments).

```
('HST hh NREFF',I5)NREFF
```

The number of reflections found by **FINDPK** in this histogram. This is the number in the "EXPNAM".REFFhh reflection file.

```
('HST hh NRRMFL',2X,A66)SCDNORMFILE
```

The name of the data normalization file for this histogram of SCD data. This file contains the incident spectra and the detector nonuniformity correction data. This file is written by **DNORMS** and is read by **NORMS**.

```
('HST hh REDHS',A) 'T run at hh:mm:ss on dd-mmm-yy'
```

Date and time that this SCD histogram was introduced into the **GSAS** system. This record is written by **REDHST**.

```
('HST hhCHI   ',F10.3)CHI
```

This record gives the diffractometer setting angle, χ, for this histogram. Data is written by **REDHST** and read by **INSTDAT**.

```
('HST hhDETA'  ,F10.3)DETA
('HST hhDETD  ',F10.3)DETD
```

These records give the nominal 2Θ angle for the SCD detector and the distance of the detector center from the sample. These records are written by **REDHST** and they are read by **INSTDAT**.

```
('HST hhDMPTIM',A)
```

This record is written by **REDHST** and gives the time that this histogram was dumped by the SCD instrument.

```
('HST hhELAPSD',I10)ELAPSD
('HST hhEVENTS',I10)EVENTS
```

These records are written by **REDHST** and gives the elapsed time for the data collection of this histogram and the number of events (counts) in the histogram.

```
('HST hhFILTYP',2X,A8)FILTYP
```

This record is used to differentiate between the several types of SCD histograms that are supported by **GSAS**. The record is written by **REDHST** and read by **INSTDAT**.

```
('HST hhHGMCNT',I10)HGMCNT
```

This is the total count in an SCD histogram, it is written by **REDHST**.

```
('HST hhIRUN  ',I5)RUN
```

The SCD data run number, written by **REDHST**.

```
('HST hhISCALE',F10.5)ISCALE
```

The scaling factor used to place this histogram on the same relative scale as the first histogram in the set. This scale is determined from the ratio of the total monitor count in the first histogram to that of the current histogram. The record is written by **INTEGRATE**.

```
('HST hhMONCNT',I10)MONCNT
```

The total monitor count for this SCD histogram. It is written by **REDHST**.

```
('HST hhOMEGA 'F10.3)OMEGA
```

This record gives the diffractometer setting angle, ω, for this histogram. Data is written by **REDHST** and read by **INSTDAT**.

```
('HST hhPHI   ',F10.3)PHI
```

This record gives the diffractometer setting angle, ϕ, for this histogram. Data is written by **REDHST** and read by **INSTDAT**.

```
('HST hhSCLRnn',I10,A)SCLR,NAME
```

These records contains the scaler data collected with the histogram. They are written by **REDHST**.

```
('HST hhTBIN  ',F10.2)TBIN
```

The record contains the length of a clock tick in microseconds. It is written by **REDHST** and is read by **INSTDAT**.

```
('HST hhTIMDLY',F10.2)TIMDLY
```

The time delay in microseconds before starting the data collection on the SCD instrument. This record is written by **REDHST** and is read by **INSTDAT**.

```
('HST hhTIMEnn',10I6)(TIME(I),I=1,WLNUM)
```

This SCD data record gives the number of clock ticks from the start of data collection to the end of the current bin. The data is written by **REDHST** and read by **INSTDAT**.

```
('HST hhTLIMIT',F10.2)TLIMIT
```

The time at which the TOF data collection scan is stopped on SCD in microseconds. This is identical to TIMDLY+TBIN*TIME(WLNUM). The record is written by **REDHST** and read by **INSTDAT**.

```
('HST hhTOTCNT',I10)TOTCNT
```

The total count in the histogram and monitor spectra for this histogram. The record is written by **REDHST**.

```
('HST hhTZEROS',F10.0)TZEROS
```

This SCD data record contains the total number of neutron pulses which were used to collect this histogram. The data record is written by **REDHST** and is read by **HSTPLOT** which uses it to determine the apparent instantaneous count rate in the area detector on SCD.

```
('HST hhWLMAX ',F10.3)
('HST hhWLMIN ',F10.3)
```

These records give the range of neutron wave lengths used in collecting this histogram. The data are written by **CELLLSQ** when the lattice constants and crystal orientation information are refined.

```
('HST hhWLNUM ',I5)WLNUM
('HST hhXNUM  ',I5)XNUM
('HST hhYNUM  ',I5)YNUM
```

The number of data channels in this histogram in the *x*, *y* and time or wave length directions. These data are written by **REDHST** and read by **INSTDAT**.

Soft constraint histogram records

In the special case of a histogram consisting of expected interatomic distances with esd's the histogram consists of the following three record types. The histogram type is 'RSN '.

```
('HST hh FACTR',G15.6)FACTR
```

The multiplier for the contributions from this histogram to the minimization function. This can be used to control the influence of the "soft constraints" on the refinement. Zero is a permissible value which results in weighting the restraints at approximately the same level as the other data, i.e. it sets the value of FACTR to the goodness-of-fit (reduced χ^2).

```
('HST hh NBNDS',I5)NBNDS
```

The number of expected interatomic distances for this histogram.

```
('HST hhBNDnnn',8I3,2F6.3)
                   IPHAS,ATSER1,ATSER2,ISYM,ILATT,IA,IB,IC,DIST,ESD
             n = 0,NBNDS
```

The expected interatomic distance with esd from atom ATSER1 to ATSER2 after application of symmetry operator number ISYM, the lattice translation number ILATT and the unit cell translations IA,IB and IC.

Single crystal instrument data records

The following records characterize the single crystal diffractometer used in the experiment. Currently **GSAS** is limited to a single instrument description for such instruments. Some of these records are unique to TOF neutron single crystal instruments while others apply to all single crystal instruments.

```
('INST   DFIL',2X,A66)
```

Name of the experiment file upon which the values in the instrument parameter file are based. This record was originally written by **INSTLSQ** when the instrument parameters were last updated.

```
('INST    IFIL',2X,A66)
```

Name of the instrument parameter file which was read into this experiment.

```
('INST   NAME ',2X,A66)NAME
```

A title entered in the instrument parameter file to provide further identification of the file.

```
('INST   RDATE',2X,A66)
```

Date and time of the last instrument parameter refinement.

```
('INST  ATTNww',7F9.0)WAVE,(ATTN(I),I=1,6)
```

The six attenuator coefficients for the CAD4 instrument. There is a set for each of the standard wavelengths (ww = CU, MO, etc.). This record can be edited by **CAD4RD** and is used by that program to correct the reflection intensities upon initial input.

```
('INST  BCHI  ',2F10.3)BCHI,SIGBCHI
('INST  BDETA ',2F10.3)BDETA,SIGBDETA
('INST  BDETD ',2F10.3)BDETD,SIGBDETD
('INST  BOMGA ',2F10.3)BOMGA,SIGBOMGA
```

These data records give the biases on the angles and detector distance needed to establish the true zero points and their estimated errors for the instrument. These data are obtained by least squares refinement of reflection position data obtained from a small standard sample (i.e. a ruby sphere). The data are copied from the instrument parameter file by **GSCDINST** and are read by **INSTDAT**. They are updated by **INSTLSQ** which can be used to modify an existing instrument parameter file or write a new one.

```
('INST  CHID  ',2F10.3)CHID,SIGCHID
```

The angle that the plane containing the detector center and the incident beam makes with the plane normal to the instrument ω axis. This angle is refinable in the program **INSTLSQ**. The record is read by **INSTDAT**.

```
('INST  CHIR  ',F10.5)CHIR
('INST  OMGR  ',F10.5)OMGR
('INST  PHIR  ',F10.5)PHIR
```

The sense of each of the rotation axes χ, ω and ϕ; +1 for right handed rotation and -1 for left handed rotation about the standard coordinate axes with the single crystal goniometer in the reference orientation. The standard coordinate axes are centered at the sample with the x-axis pointing toward the source and the z-axis pointing along the ω axis away from the goniometer drive (usually "up"). The goniometer reference orientation has the ϕ-axis coincident with the ω-axis and the standard z-axis and the χ-axis is coincident with the x-axis. These records are only needed for single crystal histograms.

```
('INST  DETA  ',2F10.3)DETA,SIGDETA
('INST  DETD  ',2F10.3)DETD,SIGDETD
```

The effective 2Θ value and its sigma of the SCD detector center. Refined and written to the instrument parameter file by **INSTLSQ**.

```
('INST  FILTYP',2X,A8)FILTYP
```

The flag differentiating the various SCD data formats.

```
('INST  L1    ',2F10.3)XTALD,SIGXTALD
```

The distance from the source, moderator, to the crystal in millimeters on the SCD instrument. This is the initial flight path length. It is refined and written by **INSTLSQ**.

```
('INST  PHID  ',2F10.3)PHID,SIGPHID
```

The angle of rotation the detector about the line from the crystal to the detector center. This angle is refined and written by **INSTLSQ**.

```
('INST  TBIN  ',F10.3)TBIN
```

Length of a clock tick used for the instrument parameter data collection. Written by **INSTLSQ**, normally not used elsewhere.

```
('INST  TZERO ',F10.3)TZERO
```

The zero-time offset for SCD data. This value is refined by **INSTLSQ** which writes it to the instrument parameter file.

```
('INST  WLBOX ',I5)
```

A flag defining the type of time binning used for SCD data.

```
('INST  XBIAS ',2F10.3)XBIAS,SIGXBIAS
('INST  XWDTH ',2F10.3)XWDTH,SIGXWDTH
('INST  YBIAS ',2F10.3)YBIAS,SIGYBIAS
('INST  YHGT  ',2F10.3)YHGT,SIGYHGT
```

The SCD detector miscentering and height and width values and their sigmas. These values are refined by **INSTLSQ** which writes them to the instrument parameter file.

```
('INST  XNUM  ',I5)XNUM
('INST  YNUM  ',I5)YNUM
```

These nominal values of XNUM and YNUM are the values for the last experiment used to revise the instrument parameter file. They were written by **INSTLSQ** to the instrument parameter file and copied to here by **REDHST**. It may have been rewritten by **INSTLSQ**.

Constraint records

The next set of records are the constraints relating the parameters to the set of variables actually refined by the least squares. These constraints are edited by routines called by each of the parameter editing routines in **EXPEDT**.

```
('LEQV ccccc  ',10I5)EQVNO,(NREC(I),I=1,EQVNO)
```

This record gives the number of equivalence constraints and the number of terms each for the overall parameter cccc. The overall parameter names are 'ABSC ', 'BKnn ', 'DIFA ', 'DIFC ', 'EXTP ', 'EXTn ', 'FP c ', 'FPPc ', 'HSCL '', 'LAM1 ', PFnn '', POLA ', 'PRFO ', 'RMTN '', 'SCAL ', 'KRAT 'and 'ZERO '.

```
('LEQV ccccnnm',3(2X,A8,F10.3))(CONSTR(I),VALUE(I),I=1,NEQV)
            n = 1 to EQVNO and m = 1 to NREC(n)
```

These records give the individual constraint terms for the overall parameter cccc, where CONSTR is a character string giving the range of histograms (as 'h') or phases and histograms (as 'p,h') whose overall parameters 'cccc' are to be constrained and VALUE is the coefficient. Allowed strings for 'p' and 'h' are 'a' for a single histogram or phase, 'a:b' for a sequence from 'a' to 'b' where 'a' and 'b' are integers and 'ALL' for all histograms or phases. For example '2:4,ALL' refers to phases 2 through 4 for all histograms. In the case of 'RMTN' constraints, CONSTR is the character string 'p   RMij', where 'p' is the phase number and 'ij' is the reciprocal metric tensor indices for the element to be constrained.

```
('LEQV HOLDBhh',6(2X,A8))(PNAM(I),I=1,N)
```

This record gives the parameter names of any background coefficients for histogram 'h' that are not to be refined. A maximum of six background coefficients can be held constant for each histogram.

```
('LEQV HOLDL p',6(2X,A8))(PNAM(I),I=1,N)
```

This record gives the names of any reciprocal metric tensor elements for phase 'p' that the user requires to be fixed beyond those that are fixed by symmetry.

```
('LEQV HOLDpnn',6(2X,A8))(PNAM(I),I=1,N)
             n = 1,(NHOLD-1)/6+1
```

These records list those atom parameters for phase 'p' that the user requires to be fixed beyond those that are to be fixed by symmetry.

```
('LNCNnnnnmmmm',2X,4(A8,F8.4))((PNAM(I,J),CNST(I,J),J=1,NTRM),
                                      I=1,NCON)
         n = 1 to NCON and m = 1 to (NTRM-1)/4+1
```

where NCON is the number of constraints, NTRM is the number of terms in each constraint, PNAM is the parameter name and CNST is the coefficient. The parameter name is constructed from the phase, atom numbers and the individual variable name. For example, `'1   2FRAC'`, refers to phase 1, atom 2 and atom fraction.

ORTEP records

The next set of records are written by **ORTEP** and hold the last set of atoms and bonds to be drawn by that program for phase 'p'.

```
('ORTp   NATOM',I5)NATOM
```

The number of atom designator codes to be found on the `'ORTp   ATMSnn'` records.

```
('ORTp   NBOND',I5)NBOND
```

The number of bond descriptor records to be found on the `'ORTp   BONDnn'` records below.

```
('ORTp  ATMSnn',6F10.0)(ADR(I),I=1,NATOM)
             n = 1,(NATOM-1)/6+1
```

The atom designator codes for the atoms to be drawn by **ORTEP**. An atom designator code 'aaacccss' is composed of three parts; the first, 'aaa', is an atom serial number, the second, 'ccc', is the unit cell designators along a,b and c for the location of the atom and the third, 'ss', is a symmetry operator designator.

```
('ORTp  BONDnn',5I5,3F10.4)IOR1,IOR2,ITAR1,ITAR2,IBOND,DMIN,DMAX,RADI
             N = 1,NBOND
```

A bond descriptor record. The bond starts at atom serial numbers IOR1 to IOR2 and ends at atom serial numbers ITAR1 to ITAR2, the bond is drawn with twice IBOND lines over the range of DMIN to DMAX bond lengths using a stick of RADI Å in radius.

Rigid body records

The next set of records occur when a rigid body is described as part of the structural model in any of the phases. These begin with descriptions of the rigid bodies in Cartesian space and are independent of the crystal structure in which they occur.

```
('RGBD  NRBDS  ',I5)NRBDS
```

The number of rigid bodies to be described.

```
('RGBD n NATR ',I5)NATR
```

The number of atoms in rigid body 'n'.

```
('RGBD n NBDS ',I5)NBDS
```

The number of times this rigid body is used in all phases.

```
('RGBD n NSMP ',I5)NSMP
```

The number of translation operators (symmetry parameters) needed to build the rigid body.

```
('RGBD nmPARM ',F10.5,2I5)SDIST,IVAR,IDAMP
        m = 1,NSMP
```

The magnitude of the translation operator 'm', the variable number in the least-squares matrix and damping flag. The variable number can be either unique or the same as another translation operator magnitude in which case they will be taken as the same least squares variable.

```
('RGBD nmSCiii',3F10.7)TRX,TRY,TRZ
             i = 1,NATR and m = 1,NSMP
```

Three translation operators on Cartesian xyz axes for atom 'i', these are multiplied by SDIST from the associated `'RGBD nmPARM '` record to give the new atom location in Cartesian coordinates. The NSMP translation operators are successively applied to the NATR atoms to complete the rigid body. Each of the NSMP operations has its own SDIST multiplier, least-squares matrix location and damping factor.

The rigid bodies defined in Cartesian space are placed in crystallographic space for each phase where needed by the following records.

```
('RGBDpn  NBDS',I5)NBDS
```

The number of times rigid body type 'n' occurs in phase 'p'.

```
('RGBDpnr  NDA',I5)NDA
```

The atom sequence number for the first atom of rigid body 'r'. All atoms in a rigid body are stored in the experiment file in sequential locations. There must be 'NATR' atoms in the atom list with serial numbers in sequence starting with 'NDA'. These atoms can not be part of any other rigid body.

```
('RGBDpnr BDFL',9I5,9I1)
                  (IBDORI(I),I=1,6),(IBDLOC(I),I=1,3)(IDAMP(I),I=1,9)
```

Least-squares matrix locations, variable numbers, for the six rotational variables and the three translational variables and their respective damping flags. The variable numbers are normally unique, but they may be the same as the variable numbers for another variable of the same type in which case they will contribute to the same terms in the least-squares matrix and have the same shifts are applied to each of them.

```
('RGBDpnr BDLC',3F10.7)BDLOC(I),I=1,3)
```

Three fractional unit cell coordinates for the location of the rigid body origin. The IBDORI codes are used to control their inclusion in the least-squares matrix.

```
('RGBDpnr BDOR',6(F8.3,I2))(BDORI(I),JAXIS(I),I=1,6)
```

The six rotations and their respective axes about the rigid body origin. These rotations operate on the Cartesian coordinate system associated with the rigid body. The axes are the three reference axes x,y and z represented by 1,2 and 3, respectively. The reference coordinates are coincident with the unrotated rigid body Cartesian coordinate system and are aligned with the crystallographic coordinate system so that *x* is parallel to *a*, *z* is parallel to *a*x*b* and *y* is parallel to (*a*x*b*)x*a*. The atomic coordinates are then generated by applying the six rotations to the rigid body coordinates, transforming the result to crystallographic fractional coordinates and finally placing origin of the rigid body at BDLOC in the unit cell.

```
('RGBDpnr LSTF',I5)LSTF
```

The thermal motion model flag. If it is zero the thermal motion for each atom in the rigid body is represented by either one U_{iso} or six u_{ij}. Those parameters are given with the atom coordinates on the `'CRSp  ATmmmB'` records. If LSTF is 1 then the thermal motion for the entire rigid body is represented by the TLS tensor which is given on the next set of records.

```
('RGBDpnrTLSF1',20I3)(ITLS(I),I=1,20)
```

Least-squares matrix locations for the six T and L matrix variables and the eight S variables. The variable numbers are normally unique, but they may be the same as the variable numbers for another variable of the same type in which case they will contribute to the same terms in the least-squares matrix and have the same shifts are applied to each of them. These values are not checked by GSAS for consistency with constraints which arise due to crystallographic symmetry.

```
('RGBDpnrTLSP1',6F8.4,2F8.2)(TLS(I),I=1,8)
('RGBDpnrTLSP2',4F8.2,4F8.4)(TLS(I),I=9,16)
('RGBDpnrTLSP3',4F8.4)(TLS(I),I=17,20)
```

The six T matrix elements, the six L matrix elements and the 8 unique S matrix elements for the thermal libration tensor for the rigid body. The format changes are to accommodate the different scales of values for the three matrices. The T matrix elements are in Å^2, the L matrix elements are in degrees^2 and the S matrix is in degree-Å.

The last record

```
('ZZZZZZZZZZZZ  Last EXP file record')
```

This is the last record in any experiment file. Its presence is checked each time the file is opened by any program in **GSAS**. If it is absent the program terminates with an error because the integrity of the file is questionable.

Handling of EXPNAM.EXP File by GSAS

When the experiment file is opened by one of the routines in **GSAS** that is capable of extensively modifying its contents (**EXPEDT** or **GENLES**), a new version is usually produced. The new version is then modified either interactively (as by **EXPEDT**) or updated (as by **GENLES**) to reflect the new values. The next routine in **GSAS** to access the experiment file then opens this new version. In essence these two routines in **GSAS** operate on the experiment file in much the same way as many system routines (e.g. EDIT/EDT in VMS or vi in UNIX). The other routines that only slightly modify the contents of the experiment file (i.e. **FOURIER**, **POWPREF, ORTEP**) and those that just read the contents (i.e. **POWPLOT**, **FORPLOT**) do not make new versions.

EXPNAM.REFnnx - The Reflection Files

These are files which contain a set of reflections for each histogram entered in the experiment file. The filename extension contains the histogram number 'nn' and a letter 'x' indicating the type of reflection information in the file. For powder data 'x' is 'P', for single crystal data 'x' is 'S', for **FINDPK** output reflections 'x' is 'F' and for merged single crystal data 'x' is 'M'. It is an unformatted direct access file; each record contains up to 36 data items.

For powder data there are 18 data items stored for each reflection

DATA(1) = HKL(1)	h index
DATA(2) = HKL(2)	k index
DATA(3) = HKL(3)	l index
DATA(4) = MUL	reflection multiplicity
DATA(5) = ICODE	reflection code
DATA(6) = PRFOCOR	preferred orientation correction
DATA(7) = DSP	d-spacing
DATA(8) = LAM	incident wavelength
DATA(9) = FOSQ	observed F_o^2
DATA(10) = SIGFO	esd in F_o^2
DATA(11) = FOTSQ	F_o^2 corrected for extinction and on scale of F_o^2
DATA(12) = FCSQ	F_c^2 with scale and extinction applied
DATA(13) = FCTSQ	F_c^2 on absolute scale
DATA(14) = PHAS	phase angle for reflection (0-360°)
DATA(15) = TRANS	transmission factor
DATA(16) = EXTCOR	extinction correction
DATA(17) = PROFLP	sum of profile function
DATA(18) = TOF	time-of-flight

For powder data **POWPREF** writes the front, center and ending TOF or 2Θ for each reflection in DATA(11)-DATA(13); these are overwritten by **GENLES** for those reflections that fall within the powder pattern. The reflection code, ICODE, contains flags indicating the status of the reflection. For refinement ready powder data it is

ICODE = IPHAS*1000 + ILAM*100 + 10*NUCORMAG + IUSE

where

IPHAS is the number of the phase for the reflection,

ILAM is wavelength flag

=0 for TOF data or reflections arising from radiation of wavelength LAM1

=1 for wavelength LAM2

NUCORMAG is a flag indicating the status of a magnetic reflection

=1 space group allowed rmagnetic reflection

=2 space group extinct magnetic reflection

IUSE is a flag giving symmetry information about F_o

=1 for space group allowed reflections

=2 for space group extinct reflections

For single crystal diffraction data ('x' is 'S') all 36 data items in the following list are used, for merged ('x' is 'M') only the first 22 items are used and for **FINDPK** data ('x' is 'F') only the first 21 are used.

DATA(1)	= HKL(1)	h index
DATA(2)	= HKL(2)	k index
DATA(3)	= HKL(3)	l index
DATA(4)	= MUL	reflection multiplicity
DATA(5)	= ICODE	reflection code
DATA(6)	= INCDNT	incident intensity for reflection position on TOF area detector
	= PSI	ψ angle for data from a standard 4-circle instrument
DATA(7)	= DSP	d-spacing
DATA(8)	= LAM	incident wavelength
DATA(9)	= FOSQ	observed F_o^2
DATA(10)	= SIGFO	esd in F_o^2
DATA(11)	= FOTSQ	F_o^2 corrected for extinction and on scale of F_o^2
DATA(12)	= FCSQ	F_c^2 with scale and extinction applied
DATA(13)	= FCTSQ	F_c^2 on absolute scale
DATA(14)	= PHAS	phase angle for reflection (0-360°)
DATA(15)	= TRANS	transmission factor
DATA(16)	= EXTCOR	extinction correction
DATA(17)	= WTFO	weight for F_o^2 used in least squares
DATA(18)	= TOF	time-of-flight
	= PHI	diffractometer angle for crystal orientation
DATA(19)	= XDET	X detector position on TOF area detector
	= CHI	diffractometer angle for crystal orientation
DATA(20)	= YDET	Y detector position on TOF area detector
	= OMEGA	diffractometer angle for crystal orientation
DATA(21)	= PEAK	single crystal integrated intensity
DATA(22)	= TBAR	absorption weighted mean path through the crystal
DATA(23)	= PKFRAC	fraction of peak included in the integration of SCD data
DATA(24)	= SIGMAI	esd on PEAK
DATA(25-27)	= SCR1	incident beam direction
DATA(28-30)	= SCR2	scattered beam direction
DATA(31-33)	= FAMAG	Real part of the magnetic structure factor
DATA(34-36)	= FBMAG	Imaginary part of the magnetic structure factor

For single crystal data of all types the reflection code is

ICODE = IPHAS*10000 + IELEM*1000 + IMAG*100 + IFRD*10 + IUSE

where

IPHAS is the number of the phase for the reflection
IELEM is the crystallite element number
IMAG is a flag indicating the status of a magnetic reflection
= 1 space group allowed magnetic reflection
= 2 space group extinct magnetic reflection
IFRD is a Friedel pair flag
= 1 for reflection with "standard indices"
= 2 for the Friedel related reflection
IUSE is a flag indicating the status of a nuclear or x-ray reflection
= 1 for space group allowed reflections
= 2 for space group extinct reflections
= 3 space group allowed magnetic reflection with fractional indices
= 4 space group extinct magnetic reflection with fractional indices

This file is opened by **OPNREFx**, written by **WRTREFx** and read by **REDREFx** where **x** is **P**, **S** or **F**. The 'M' type files are opened, read and written by the **'S'** routines.

EXPNAM.Phh - The Histogram Files

There is a histogram file 'EXPNAM.Phh' for each powder histogram in the experiment file, and the value of hh matches the histogram number. These files are blocked, unformatted, direct access files; each "record" consists of

ICODE	profile point status code
T	time of flight in µsec or 2Œ in centidegrees. The position is the center of the channel for TOF data.
YO	total observed intensity
YC	calculated intensity excluding fixed background
YI	incident intensity
YB	fixed background intensity
YW	weight
CW	channel or step width in same units as T
IOVLP	reflection range code

The profile point status code is a bit pattern with the following definitions

BIT(0)	- 1	profile point has only background intensity
BIT(0)	- 0	profile point has reflection contributions
BIT(1)	- 1	profile point is in excluded region
BIT(1)	- 0	profile point is in usable region
BIT(2-10)	- 1	profile point coincides with reflection position
BIT(2-10)	- 0	profile point not at reflection position

The bit number for the peak position markers, BIT(2-10), are IPHAS+1. These are used by the plotting program, **POWPLOT**, to mark the reflection positions for each phase. These codes are generated by **HSTPROC** and **HSTMACH** in **POWPREF**.

The reflection range code, IOVLP, is given by

```
IOVLP = CHIGH*16384 + CLOW
```

where CLOW and CHIGH are the first and last, respectively, reflection numbers that contribute to the profile point. These are determined by **HSTMACH** in **POWPREF**. Obviously, the reflections that contribute may come from different phases; they are all mixed together in ascending order of TOF or 2Θ of their leading edges in the reflection file.

These "records" are entered into an array by **WRITPRF**; when full the block is written to the histogram file. Similarly, the "records" are read from the array by **READPRF**; if a requested "record" is not in the current array a new block is read from the file.

EXPNAM.CMT - Variance-Covariance File

The variance-covariance information required by **DISAGL** is written as a sequential unformatted file by **WRCOVAR**. It is read by **RDCOVAR**. These routines also open this file. The old version of this file, if it exists, is deleted by **WRCOVAR** and a new one is created and written. The file consists of three large logical records each of which is described below.

```
NCYCLE,NUMPAR,(PARNAMS(I),I=1,NUMPAR),NUMVAR,(VARNAMS(I),I=1,NUMVAR)
```

The first logical record contains the least squares cycle number, the number of refinable parameters and their names, and the number of resulting least squares variables and their names. The number of variables can be less than the number of parameters because some parameters may be made equivalent by symmetry or user constraints.

```
MATSIZ,(AMAT(I),I=1,MATSIZ)
```

The second logical record contains the size of the variance-covariance matrix and its elements.

```
NCNSTS,(IJCNMT(I),CONMAT(I),I=1,NCNSTS)
```

The third logical record contains the number of non-zero elements in the combined symmetry and user constraint matrix, their indices and associated values. This is a sparse matrix description where only those elements with explicit non-zero values are given; the other elements are omitted.

EXPNAM.fmp - Fourier Map Files

The Fourier map files are unformatted direct access files written by **FOURPRT4** during the calculation of the maps by **FOURIER**. There is one of these for each possible kind of map; they have different extensions. The extensions are FOBS, FCLC, DELF, PTSN and DPTN which correspond to the available map types. **FOURPRT4** also opens these files; any old version is deleted and a new one written. They are read by **REDFMP** as part of **FORPLOT**, **FORPLT** in **PLOTTER** and **FRSHR** in **FORSRH**. These files consists of two header records followed by a set of data records, one for each map 'slice'.

```
NAME,MAPTYP,(CELL(I),I=1,7)
```

The first header record contains a 66 character title, the map type (FOBS, etc.) as a 4 character code (also used for the extension), and the lattice parameters and unit cell volume. This record is skipped by **REDFMP**, all other routines read it.

```
(NXYZI(I),I=1,3),(NXYZO(I),I=1,3),(NXYZT(I),I=1,3),
                    MSECT,NRHO,RMAX,RMIN,SRHO
```

The second header gives the number of steps along the cell edges, the starting step position, the number of steps computed, an orientation flag and the number of density values per slice. The last three values are the maximum and minimum density and the sum of all the density values in the map. The step information is presented as for a hypothetical map section with the first value for across the map, the second value down the map and the third value for section to section. The orientation flag indicates which crystallographic axis is not in the sections.

```
(RHO(I),I=1,NRHO),ROMX,ROMN
```

This record contains the NRHO density values for a section and the maximum and minimum density in the section. There is one of these records for each section in the map.

GSAS Standard Powder Data File

The input powder data file for **GSAS** is a direct access, fixed record length file. It contains a few header records followed by blocks of data each corresponding to an individual powder pattern. Each block is preceded by its own header. All records must be 80 characters in length. The main header has one or two records:

```
(80A)TITLE
```

A title record is first; the information is used by **GSAS** for titles only. **GSAS** can only use the first 66 characters of this record but it must be filled out to 80 characters.

```
('Instrument parameter',60A)FNAME
```

An optional record that must start with the 20 characters shown followed by the instrument parameter file name. If this record is omitted, **GSAS** requests this file name from the user in **EXPEDT**.

Then follows a number of data blocks each beginning with a header. The header record is in free format and has different forms depending on the type of data that follows it. For standard type data the header is:

```
('BANK',3I,A,4F,' STD')IBANK,NCHAN,NREC,BINTYP,(BCOEF(I),I=1,4)
```

The fields are separated by spaces and 'BANK' must be upper case. IBANK is the bank number; if it is zero the data block is from the incident beam monitor. The value of IBANK must be unique within a data file. For TOF data the value of IBANK must corrrespond to the bank number found in the instrument parameter file for the detectors which produced the data. This correspondence is not needed for CW data. NCHAN is the number of data points in the block of data and NREC is the number of records. There are 10 data points per record so NREC is NCHAN/10 rounded up. The value of BINTYP depends on the way the stepwidths are determined. This format is suitable only when the esd associated with each profile point can be calculated directly from the given intensity (i.e. $\sigma_I = \sqrt{I}$). If the esd can not be obtained in this way, then one of the other data formats which explicitly input the esd should be used (see below).

If BINTYP is 'CONST' then the data has a constant stepwidth; BCOEF(1) is the offset for the first step and BCOEF(2) is the stepsize, both in microseconds or centidegrees. If BINTYP is 'LOG6' then the data has a specific logarithmic scaling for the stepwidth; BCOEF(1) is the offset in microseconds and BCOEF(2) is either 102.4 or 409.6 which is the allowed stepsize increment for the Los Alamos Model 6 TOF clock. If BINTYP equals 'TIME_MAP' then a complete time map which defines the step sizes and positions is read from another section of this file (see below) and BCOEF(1) is the number of the time map to be read. If BINTYP is 'LPSD' then BCOEF(1) is the nominal 2Θ value in centidegrees for the linear position sensitive detector (LPSD), BCOEFF(2) is the channel number for this 2Θ angle, and BCOEF(3) is the width of one channel in centidegrees at this position.

Usually CW data has BINTYP equal to 'CONST' or 'LPSD' and TOF data can be any one of the BINTYP's mentioned above except 'LPSD'.

This header is followed by 'NREC' records containing the data in the following format.

```
(10(I2,F6.0))(NCTR(I),YO(I),I=1,NCHAN)
```

where NCTR is the number of counters used to collect the data for each step and YO is the number of counts per counter observed. If NCTR is zero or missing then it is assumed to be one.

The first alternate form for the header is designed to handle data which has been corrected for some instrumental effects (incident intensity, absorption, etc.) so that the weights can no longer be derived directly from the intensities. The header is:

```
('BANK',3I,A,4F,' ESD')IBANK,NCHAN,NREC,BINTYP,(BCOEF(I),I=1,4)
```

As above the value of IBANK must be unique within a data file. Each data point consists of the intensity and an esd for that intensity. Thus there are 5 data points per record and NREC is NCHAN/5 rounded up. The values of BINTYP and BCOEF are the same as described for the standard data header.

The data records are in the following form:

```
(10F8)(YOT(I),YE(I),I=1,NCHAN)
```

where YOT is the intensity and YE is the esd for YOT. The decimal point must be given to force its proper placement in these values.

The second alternate form for the header is designed to handle data which has been collected on a diffractometer where the steps between values is somewhat uneven (e.g. TOF data collected on the diffractometers at the ISIS Facility, Rutherford-Appleton Laboratory, UK) The header is:

```
('BANK',3I,A,4F,' ALT')IBANK,NCHAN,NREC,BINTYP,(BCOEF(I),I=1,4)
```

As above the value of IBANK must be unique within a data file. For TOF data the value of IBANK must corrrespond to the bank number found in the instrument parameter file for the detectors which produced the data. This correspondence is not needed for CW data. Each data point consists of the TOF, intensity and an esd for that intensity. Thus there are 4 data points per record and NREC is NCHAN/4 rounded up. The values of BINTYP and BCOEF are the same as described for the standard data header with the addition of BINTYP = 'RALF' which forces the use of the TOFT values below for the positions. In this case BCOEF(1) is the starting TOF in μsec*32, BCOEF(2) is the width of the first step in μsec*32, BCOEF(3) is the start of the log scaled step portion of the data in μsec*32 and BCOEF(4) is the resolution to be used in approximating the size of each step beyond BCOEF(3).

The data records are in the following form:

```
(4(F8.0,F7.4,F5.4))((TOFT(I),YOT(I),YE(I),I=1,NCHAN)
```

where TOFT is in microsteps (TOF in pulses of width CLCKWDT times 32 or centidegrees times 32), YOT is the normalized count and YE is the esd for YOT. Normally the decimal point is left off the values and the format statement properly scales the values.

A time map is included in the file by starting with the following header:

```
('TIME_MAP',3I,A,F)MAPNO,NVALS,NREC,'TIME_MAP',CLCKWDT
```

The fields are separated by spaces and 'TIME_MAP' must be uppercase. MAPNO is the time map number. NVALS is the number of data items in the time map; there are three for each point in the map. NREC is the number of records which is NVALS/10 rounded up. CLCKWDT is in number of clock pulses per µsec.

This header is followed by NREC records which contain the time map information.

```
(10I8)((TMAP(J,I),J=1,3),I=1,MAXMAPU),TMAX
```

where MAXMAPU is NVALS-1, TMAP is a triplet of time map values and TMAX is the maximum allowable TOF. The three time map values are starting channel number, TOF in pulses of width CLCKWDT for the front of the channel and the channel width in pulses. Each change in the channel width in the data set has a corresponding entry in the time map; the entries are in ascending order of channel number. Currently there are 1024 entries allowed for the time map in **GSAS**.

These sets of header record plus data records may be repeated in any order until the entire data set for the experiment is included in the file. This file is processed by **HSTREAD** for **POWPREF** and **READHST** for **EXPEDT**; the data header records are interpreted by **EXTRBNK**, the data records are read by **GETRAWPT** and the time map is read by **REDTMAP**.

ATOMDATA.DAT - Atom Data File

The characteristic atomic information (scattering factors, absorption coefficients, etc.) are stored on a formatted ISAM file. Each record is 80 characters long and starts with a 12 character key which is used by **GSAS** to fetch that record from the file. The information on the record is read as a 66 character block by **TYPINS** and written unchanged on to the 'AFAC' records in the experiment file. The file is arranged so that all information for a given element is in one place on four different kinds of records. A description of each kind follows. There are several records at the beginning of the file listing the various references used to accumulate the data.

```
('zz aaaa      ',9F7.0)(SCFC(I),I=1,9)
   z = atomic number, a = element symbol
```

This record holds x-ray scattering factor coefficients (a_i, b_i and c) as listed by Cromer & Waber (1974), International Tables for X-ray Crystallography, Vol. IV, p 99-101. The atomic number is an integer in the range 1-99; this is the same for all records for a given element. The element symbol consists of the standard two letter chemical symbol (upper case) and the valence as a sign and a numerical value, e.g. 'TI+4', if necessary. There is always one of these records for every element giving the neutral atom scattering factors; some elements also have ionic scattering factors. The atomic scattering factor is then calculated by

$$f = c + \sum_{i=1}^{4} a_i e^{-b_i \sin^2\theta/\lambda^2}$$

```
('zz aa_nnn   ',F7.0,4F6.0)WT,BLEN,BILEN,RNMU,RNMUX
```

The isotopic data for 'aa_nnn' where 'aa' is the chemical symbol (upper case) and 'nnn' is the isotope. The data are isotopic weight, real and imaginary neutron scattering lengths, and the wavelength dependent and wavelength independent neutron absorption cross sections. If 'nnn' is blank then the data are for the natural abundance element. Synthetic elements do not have 'natural abundance' data. There may be several of these records for a given element. The values are taken from Koster & Yelon, (1982), Neutron Diffraction Newsletter.

```
('zz aa_SIZ   ',2F10.2,F5.2,I5)DRAD,ARAD,PRAD,COLOR
```

This record contains default atom size data for distance/angle calculations and for the structure plotting programs.

```
('zz aa_XAB   ',1X,5F6.0)(RXMU(I),I=1,5)
```

The x-ray absorption cross sections for Cr, Fe, Cu, Mo and Ag Kα radiation, respectively. These values are taken from Hubbell, McMaster, Del Grande & Mallett (1974), International Tables for X-ray Crystallography, Vol. IV, pp 55-66.

```
('zz aa_XAN   ',1X,10F6.0)(XFP(I),XFPP(I),I=1,5)
```

The real and imaginary parts (f' and f") of the anomalous dispersion for Cr, Fe, Cu, Mo and Ag Kα radiation, respectively. These values are taken from Cromer & Ibers (1974), International Tables for X-Ray Crystallography, Vol. IV, pp 149-150.

Instrument Parameter File

The instrument parameter file is formatted the same way as the experiment file (see above) with 80 or less character records and a 12 character key. The information on this file is the characteristic data for the instrument used to collect x-ray or neutron diffraction data. It holds the geometric description of the instrument, characteristic intensity spectrum and other specific data. The records are very similar to some of those in the experiment file; only the keys are different. A few records are not used by **GSAS** programs but are needed by local data preparation programs. Nonetheless, some of these records are ultimately copied to the experiment file; this is done in **HSTINS**. What follows is a complete listing of the records in an instrument parameters file for a TOF powder diffractometer at LANSCE with some from other types of instruments.

The initial set of records characterize the whole instrument and are not copied to the experiment file.

```
('INS   BANK  ',I5)NBANK
```

The number of counter banks on the instrument. Generally NBANK is one for CW instruments; TOF instruments usually have more than one bank of detectors. It can also indicate the number of different configurations used for the instrument (i.e. different x-ray tubes used on the diffractometer). This record is required by **GSAS**.

```
('INS   FPATH1',F10.0)FPATH1
```

The neutron flight path in meters from the source to the sample on a TOF diffractometer. Not needed by **GSAS**.

```
('INS   HTYPE ',2X,A4)HTYPE
```

The histogram type for all data from this instrument; see the description of the ' EXPR HTYPc' record in an experiment file for a full description of histogram types. For powder data the last character of HTYPE must be 'R'; the other characters specify the kind of data. This record is required by **GSAS**.

```
('INS   MONIT ',I5,F10.0,I5,F10.0)MTUB1,MPATH1,MTUB2,MPATH2
```

The spectrum numbers and location of direct beam monitors in meters as measured from the source on a TOF diffractometer. Not needed by **GSAS**.

```
('INS   NSPEC ',I5)NSPEC
```

The number of spectra collected by a LANSCE TOF diffractometer; equal to the number of tubes plus the number of direct beam monitors. Not needed by **GSAS**.

The next section of records contains specific information for a bank of detectors. They are repeated for each of the NBANK detectors on the instrument. Unless stated otherwise they are required by **GSAS**.

```
('INS bb ICONS',3F10.0, 10X,F10.0,I5,F10.0)
                  DIFC,DIFA,ZERO,POLA,IPOLA,KRATIO
       b = bank number
```

These are the diffractometer constants for one bank of detectors on a powder diffractometer. In the case of a TOF diffractometer the constants relate d-spacing and TOF in microseconds. For CW data the same record holds wavelength data, LAM1 and LAM2, in place of DIFC and DIFA. The polarization fraction POLA, the polarization type IPOLA, and the $K_{\alpha2}/K_{\alpha1}$ ratio KRATIO are absent for neutron data.

```
('INS bb IRAD ',I5)IRAD
```

If this instrument is an x-ray single crystal or powder diffractometer, this record is required and has an integer (1 to 5) indicating which characteristic radiation is used; Cr, Fe, Cu, Mo or Ag Ka, respectively. If IRAD is zero then special anomalous and absorption coefficients for each kind of atom will be required when this histogram is used.

```
('INS bbBNKPAR',5F10.0,2I5)DIST,TTHETA,TILT,SEPN,HGHT,NTUBE,ITUBE
```

This record describes a TOF counter bank. This data is mostly used by the program **FSTBUSBIN** to bin the individual spectra from the ^{3}He tubes in a bank into one spectrum. It is not needed for CW instruments.

```
('INS bbBNKTCc',8F7.2)(DIFC(I),I=1,NTUBE)
             c = 1 to 1+(NTUBE-1)/4
```

These are the individual DIFC values for each tube in a bank of detectors; if present this is used by **FSTBUSBIN** in preference to the data on the previous record. They are not needed for CW instruments and not needed by **GSAS** for any instruments.

The next series of records characterize the incident spectrum and are initially defined by the program **FITSPEC**. At least the first two are required for both TOF and CW powder instruments.

```
('INS bbI HEAD',2X,A66)IHEAD
```

A title taken from the incident spectrum raw data file. It can contain "dummy" information.

```
('INS bbI ITYP',I5,2F10.4,I10)ITYP,TMIN,TMAX,CHKSUM
```

The type of incident intensity function, the minimum TOF in msec (or 2Θ in deg), the maximum TOF (or 2Θ) over which the function can be applied and a checksum on the incident spectrum. The latter is used to check if this incident data has been applied to another histogram. For data sets for which there is no fitted incident spectrum, set ITYP to 0, choose appropriate values for TMIN, TMAX and pick a random integer for CHKSUM.

```
('INS bbICOFFc',4E15.6)(VINC(I),I=1,12)
             c = 1 to 3
```

Coefficients for the incident intensity function. For TOF they are expressed in terms of TOF in milliseconds. These records not needed if ITYP is 0.

```
('INS bbIECOFc',4E15.6)(SINC(I),I=1,12)
             c = 1 to 3
```

The esd's for each of the coefficients. These records not needed if ITYP is 0.

```
('INS bbIECORc',10F6.3)(PINC(I),I=1,78)
             c = 1 to 8
```

The elements of the correlation matrix in upper triangular form for the incident intensity coefficients. These with the esd's are used to calculate the esd in the calculated incident intensity at each point in the profile. These records not needed if ITYP is 0.

```
('INS bbPRCFn ',2I5,F10.5)PTYP,NCOF,CTOF
            n = 1,NTYP
('INS bbPRCFnc',4E15.6)(COF(I),I=1,NCOF)
             c = 1 to 1+(NCOF-1)/4
```

These records give the NTYP sets of available profile functions and their default coefficients for data from this bank of detectors. The first record contains the powder profile type , number of coefficients and a cutoff factor. The second and subsequent record (c = 1,...) contain the coefficients with four per record. The first set defines the default profile function type for this instrument, i.e. PTYP for the first set does not have to be 1.