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INTEGRATION OF OVERLAPPING PEAKS IN POSITION-SENSITIVE-DETECTOR (PSD) DATA BY LEAST-SQUARES FITTING

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Résumé - La modélisation des reflexions partiellement superposées d'échantillonnées sur un réseau multi-dimensionnel est décrite. Dans le cas de la diffraction neutronique une fonction Gaussienne multi-variable est le plus souvent convenable et elle a l'avantage d'être facilement intégrable. Le choix des coordonnées fonctionnelles et des origines possibles des composantes non-Gaussiennes dans la distribution des données sont discutées. Des exemples de modélisation des reflexions de structures cristallines modulées, et de cristaux maclés ainsi que de reflexions d'un monocristal superposées à la diffusion d'une poudre sont présentées.

Abstract - The fitting of overlapping reflections sampled on a multi-dimensional grid is discussed. In the case of neutron diffraction a multi-variate Gaussian is usually appropriate, and has the distinct advantage of being readily integrated. The choice of the functional coordinates and the possible sources of non-Gaussian components in the observed distribution are discussed. Some examples of the fitting of overlapping reflections from incommensurate structures and from twinned crystals, and of single-crystal reflections superimposed on powder scattering are presented.

I - INTRODUCTION

For non-twinned crystals of compounds in commensurate phases the reciprocal lattice spacing between consecutive reflections is constant along any chosen direction in reciprocal space. Since the instrumental resolution function varies slowly through reciprocal space, if partial overlap of reflections occurs it will do so for most consecutive pairs. It is therefore necessary at the outset to choose experimental conditions that will avoid overlap.

For incommensurate structures, however, the reciprocal lattice spacing between satellite reflections, or between each satellite reflection and the associated commensurate reflection, may be orders of magnitude smaller than the spacing between commensurate reflections. The difference in spacing often means that a compromise choice of experimental parameters is made in order both to observe a sufficient number of sets of reflections and to resolve them to some extent. A similar compromise may be necessary for twinned crystals in which the reciprocal lattices of the individual crystallites do not exactly coincide. These compromise parameters may result in partial overlap within groups of reflections, which in general will require profile fitting to extract integrated intensities and scattering angles for the individual reflections. In general the peaks are better resolved and hence the reduced data are more accurately determined if each group of overlapping reflections is sampled on a fine three-dimensional (3-D) grid of points, as obtained, for example, by scans with a 2-D PSD. The fitting would then ideally be made in 3-D, although computational limitations may constrain the fitting to 2-D or 1-D. Even in the last case careful choice of the projection of the count array can minimize the inaccuracies in the reduced data.
This paper describes the application of multi-dimensional profile fitting to the separation of overlapping neutron reflections from incommensurate structures and twinned crystals. The choices of fitting function and functional coordinates are discussed with reference to the instrumental and crystal characteristics. The integrated intensity for a 3-D Gaussian function is derived in detail. Examples in 2- and 3-D of single scans with multidetectors and of multiple scans with single detectors are presented.

II - INSTRUMENTAL RESOLUTION FUNCTION AND SAMPLE CONTRIBUTION

In this paper \( \omega \) refers to a crystal rotation about the vertical instrument axis and \( \gamma \) and \( \nu \) refer to the polar angles on the surface of the Ewald sphere; \( \gamma \) is the angle in the horizontal plane, \( \nu \) is the angle out of the plane. Lines corresponding to constant Bragg angle \( \theta \) on the Ewald sphere are given by \( \cos 2\theta = \cos \gamma \cos \nu \). The plane of diffraction of the monochromator is assumed to be horizontal, although the discussion can be applied to inclined-beam diffractometers if the instrument axis is defined to be perpendicular to the plane of diffraction of the monochromator.

The observed count distribution of a single reflection is the convolution of the instrumental resolution function with the scattering probability distribution of the sample, where the convolution variable is determined by the scan direction. The instrumental resolution function for a neutron diffractometer has been derived for different configurations by, for example, Cagliotti and Ricci /1/, Cooper and Nathans /2/ and Haywood /3/. In their cases the interest was primarily to determine the influence of the various instrumental parameters on the 1-D reflection width and to relate the observed widths and peak heights in different scan modes to the reflection structure amplitude and the mosaic spread of the sample. Here we shall determine the parameters of the distribution by fitting, so that it is only the expected functional form of the resolution function that is of interest. In any case the accuracy of a-priori calculation of the resolution function would usually be insufficient to allow accurate separation of overlapping reflections.

For a neutron diffractometer the transmission functions (in the horizontal plane) of Soller slit collimators and the mosaic spread of the monochromating crystal are usually nearly Gaussian functions of instrumental angles /4,5/. The vertical divergence however is often poorly defined, so that a Gaussian function may be less appropriate for this component. The instrumental resolution function, which is a multi-variate convolution of these components, will also be nearly Gaussian. It is necessary to be aware however of the directions along which the individual transmission and reflection probabilities of the different elements broaden the observed 3-D scattering distribution, to be able to identify from the observed distribution the sources of the non-Gaussian components. Schoenborn has discussed the effect of the different contributions from the monochromator, optical elements and the sample on the shape of neutron reflections in the \( \gamma-\omega \) plane for scans in \( \omega /6/\). Of particular relevance here are the broadening due to the beam divergence and the broadening due to the wavelength bandwidth, both of which arise from the mosaicity of the monochromator. The effect of beam divergence is directed along the \( \omega = \gamma \) line, while the effect of the bandwidth is directed along a line whose angle to the \( \gamma \) axis is monochromator and \( \gamma \) dependent. Schoenborn's analysis can also be applied to a 3-D distribution with the lines in the \( \gamma-\omega \) plane becoming planes in \( \gamma-\nu-\omega \) space which lie along constant \( 2\theta \) lines at each \( \omega \).

The effect of the scan type may be pictured as a passing of the instrumental resolution function centred on the reciprocal lattice point through the Ewald sphere along the scan direction, with the sphere smeared to account for the mosaic spread and the size of the sample. The major sample contributions to the observed distribution are the sample size and the mosaic spread. For an \( \omega \) scan the latter results in broadening along \( \omega \). Incommensurate reflections may also exhibit additional broadening in reciprocal space, e.g. along the propagation vector.

It is important to note that the relationship between a reciprocal-space coordinate system centred on the reflection and the instrumental angular coordinate system \( (\gamma, \nu, \omega) \) is a homogeneous affine transformation only in the small-angle approximation. Thus in general the resolution function in reciprocal space is not linearly related to the resolution function in instrumental coordinates. While for one reflection it
Fig. 1 - Projection onto the y-ω plane of the count distribution observed for the magnetic reflections near the 1/3 1/3 0 reciprocal lattice point of TlFeCl₃ at 1.2K. All TlFeCl₃ scans shown in this paper were performed on the multidetector diffractometer D16 at the I.L.L. The detector, which moves only in the equatorial plane, is a gas-filled 2-D flat multi-wire proportional counter 16 cm wide and 8 cm high /7/. The spacings of the 64 vertical anodes and the 16 horizontal cathodes are 2.54 mm and 5.00 mm respectively; the sample-to-detector distance for these scans was 1000 mm. Full details of the TlFeCl₃ experiment will be published elsewhere.

Fig. 2 - 2-D q-scan around the hexagonal 1 0 0 reflection of (CD₃)₄NMnBr following transformation to the multi-domain monoclinic phase /8/. The distributions in Fig. 2 and 3 were obtained from scans with a single detector along parallel lines in reciprocal space. In contrast to the multidetector case, the distributions are obtained directly on rectangular grids in reciprocal space. The contour plot shows that the individual reflection profiles are the same in extent and orientation in the instrumental coordinate system but not in reciprocal space.

Fig. 3 - 2-D q-scan around the 0 2 2 reciprocal lattice point in the β phase of quartz /9/. The six satellite peaks are inelastic precursors of the incommensurate phase that occurs 1.5° lower in temperature. A q-dependent broadening of the satellites is clearly evident.
may be possible to approximate the true resolution function in instrumental coordinates by the same function in reciprocal-space coordinates, it will not necessarily be valid to assume the same orientation and extent of the resolution function in reciprocal space for two neighbouring reflections. In the instrumental coordinate system however this assumption may be valid since the resolution function is independent of \( \omega \), nearly independent of \( \nu \), and varies only slowly with \( \gamma \); the \( \gamma \) variation arising from the wavelength spread in the monochromated beam. This is illustrated by Figs. 1 and 2.

Since the resolution of a neutron diffractometer is usually relatively poor perpendicular to the scattering plane of the monochromator, little may be lost in accuracy of the reduced data if the counts are projected onto the \( \gamma - \omega \) plane, especially if the overlap only occurs in this plane. To maintain the resolution of the reflections, the projection onto the plane should be made along the major axis of the resolution function out of this plane. This will usually be along lines of constant \( 2\theta \) at each \( \omega \) and will only be equivalent to projection along \( \nu \) near \( \nu = 0 \).

In cases of severe overlap it may be desirable to constrain all peaks in one group to have the same distribution function, in both extent and orientation, to be able to obtain a sensible fit. This is only possible if the instrumental angles are the functional parameters, and if there is no sample contribution which depends on \( q \), the reciprocal-space vector corresponding to the instrumental setting (see Fig. 3). If there is a \( q \)-dependent sample contribution it may still be possible to reduce the number of parameters by using a fitting function which is a convolution of a common resolution function and a uni-variate sample function. It may also be possible to constrain the centres of the peaks within a group to adopt a certain geometry in reciprocal space.

III - FITTING THE DISTRIBUTIONS

The observed count distributions in Section IV were fitted by a sum of uni-, bi- and tri-variate Gaussians on an inclined planar background. The general form of the calculated count at the \( j \)th point \((x,y,z)\) of the distribution is,

\[
C_j(x,y,z) = b_o + b_x x + b_y y + b_z z + \Sigma_i h_i \exp(-e_{11}^x x^2 - e_{11}^y y^2 - e_{11}^z z^2 - 2e_{12}^xy x'y' - 2e_{13}^zx x'z' - 2e_{22}^yy'y' - 2e_{23}^zy y'z').
\]

The background parameters are \( b_o, b_x, b_y \) and \( b_z \). The \( i \)th reflection has peak height \( h_i \) and is centred on the point \((x_i,y_i,z_i)\), where \( x'_i = x - x_i, y'_i = y - y_i \) and \( z'_i = z - z_i \). The parameters \( e_{kl} \) describe the extent and orientation of ellipsoidal contours of equal height.

Some terms can be omitted in special cases, e.g. if \((x,y,z) = (y,\nu,\omega)\), \( e_{xy}^2 = e_{yz}^2 = 0 \) in the equatorial plane. If the \( \nu \) projection is fitted the terms in \( y \) are omitted. Powder lines arising from, for example, the aluminium heat shields of a cryostat can be fitted by 1-D Gaussians with functional parameter \( 2\theta \).

The parameters were refined using the routine VA05A of the Harwell Subroutine Library to minimize \( \Sigma_j w_j (C_j^O - C_j^F)^2 \) where \( C_j^O \) is the observed count at the point \((x,y,z)\) and the weight \( w_j = (1/C_j^O)^2 \). For this problem the main advantage in using VA05A is that the types of functions to be fitted can be quickly modified since the derivatives are calculated numerically. It is also very robust in minimizing highly non-linear functions /11/. The main disadvantage is that a large amount of storage is required; the work array must be dimensioned to \( 2n(n + m) + 5n + 2m \) elements, where \( n \) is the number of parameters and \( m \) is the number of observations. The variance-covariance matrices of the final parameters were calculated using the subroutine SERROR /12/.
The convergence indicators are the R-factor,
\[ R = 100 \left[ \frac{\sum_{j} w_{j} (c_{j}^n - c_{j}^c)^2 / \sum_{j} w_{j} c_{j}^c m_{j}}{\sum_{j} w_{j} m_{j}} \right]^{1/2}, \]
and the goodness-of-fit,
\[ S = \left[ \frac{\sum_{j} w_{j} (c_{j}^n - c_{j}^c)^2 / (n - m)}{\sum_{j} w_{j} m_{j}} \right]^{1/2}. \]

The use of weights based on counting statistics attaches more significance to the tails of the peaks than if unit weights are used. This helps prevent the strongest reflection in a group of overlapping reflections from dominating the fit. In the 2-D examples in Section IV the magnitude of the calculation is similar to refinement of a small crystal structure; around 20 parameters to be determined by 800 observations. In these examples convergence from a reasonable starting model was obtained after typically 50 cycles which took 120 s CPU time on a DEC 10 computer. The observations are of poorer quality statistically than those in a typical small-structure refinement. This is not surprising since the 800 count observations in one complete scan contribute to just a few observed structure factors. Although values of S near 1.0 may be obtained, the R-factors are higher than in structure refinement.

Initial estimates of the background parameters were obtained from the bounding counts of each scan; initial estimates of the reflection parameters were made by inspection of the observed distributions. VA05A obtains an approximation to the first partial derivative matrix in the first n cycles. Although improvements are made to this matrix in later cycles, if the initial estimated parameters are far from the final values, a second call to VA05A may be necessary to obtain a matrix that gives satisfactory convergence.

The Gaussian functions are readily integrated by diagonalization of the symmetric matrix with elements \( e_{i1} \), to obtain the eigenvalues \( E_{i1} \), \( E_{i2} \) and corresponding eigenvectors \( v_{i1} \), \( v_{i2} \) and \( v_{i3} \) with components \( v_{i1x} \), \( v_{i1y} \), etc. The integrated intensity of the \( i \)th reflection is then,
\[ I_i = h_i \int \int \int \exp(-e_{i1} x^2 - e_{i2} y^2 - e_{i3} z^2 - 2e_{i12} xy - 2e_{i13} xz - 2e_{i23} yz) \, dx \, dy \, dz \]
\[ = h_i \frac{\pi^3}{(E_{i1} E_{i2} E_{i3})^{1/2}}. \]

The estimated standard deviation of \( I_i \) is calculated by propagation of the estimated errors in \( h_i \) and the \( e_{i1} \):
\[ \sigma^2(I_i(p_k)) = \sum_k (\frac{\partial I_i}{\partial p_k})^2 \sigma^2(p_k) + 2 \sum_k \sum_{k'} (\frac{\partial I_i}{\partial p_k})(\frac{\partial I_i}{\partial p_{k'}}) \sigma(p_k) \sigma(p_{k'}). \]

Since there is often strong correlation amongst the ellipsoid shape parameters the covariances must be included in the calculation. The partial derivatives with respect to the ellipsoid parameters can be calculated analytically: e.g.
\[ (\frac{\partial I_i}{\partial e_{i12}}) = -2h_i \int \int \int \exp(-e_{i1} x^2 - e_{i2} y^2 - e_{i3} z^2)
- 2e_{i12} xy - 2e_{i13} xz - 2e_{i23} yz) \, dx \, dy \, dz \]
\[ = -2h_i \int \int \int (x^2 v_{i1} + y^2 v_{i2} + z^2 v_{i3})(x^2 v_{i4} + y^2 v_{i5} + z^2 v_{i6})
\[ \exp(-E_{i1} x^2 - E_{i2} y^2 - E_{i3} z^2) \, dx \, dy \, dz. \]

The new coordinates \( X, Y, Z \) are related to \( x, y, z \) by the matrix of eigenvectors. The antisymmetric cross-terms in \( X, Y \) and \( Z \) vanish when the integrals are evaluated, and the right-hand side reduces to a sum of products of integrals of the form,
\[ \int_{-\infty}^{\infty} x^2 \exp(-x^2) \, dx \quad \text{and} \quad \int_{-\infty}^{\infty} \exp(-x^2) \, dx, \]
which when solved give,

$$ (\partial I_1/\partial e_{1}^{XY}) = -2I_1(v_{ix}^X v_{iy}^X/E^X + v_{ix}^Y v_{iy}^Y/E^Y + v_{ix}^Z v_{iy}^Z/E^Z). $$

Non-Gaussian modifications can be included as convolutions with functions of unit volume, thereby retaining the ease of integration.

Fig. 4 - Observed and fitted projection onto the $\gamma$-$\omega$ plane of the 0 1 0 nuclear reflection of TlFeCl$_2$. The intensity scale of the difference distribution is enlarged by a factor 4 to emphasize the mosaic tails of the sample and monochromator.

Fig. 5 - Observed and fitted projection onto the $\gamma$-$\omega$ plane of a single-crystal reflection of TlFeCl$_2$, which overlaps several parasitic powder lines.
IV - EXAMPLES

Figs. 4 to 8 show the results of fits to some nuclear and magnetic reflections of TlFeCl$_3$. The suitability of Gaussian functions to fit the projection onto the $\gamma$-$\omega$ plane is demonstrated by the fit to a strong commensurate reflection (Fig. 4), although small non-Gaussian tails in the mosaic distributions of the sample and the monochromator are readily identifiable. The fit to the 3-D distribution of the same scan was worse due to the non-Gaussian contributions to the vertical component of the resolution function ($R = 30.97$, $S = 18.04$ and higher features in the difference plot).

For the scans in Fig. 6 the centres of the overlapping reflections lie in the horizontal plane so that fits to the projections onto the $\gamma$-$\omega$ plane are sufficient.

Observed
-2/3 -2/3 0
2 peaks

Calculated
$R = 10.04$
$S = 1.97$

Difference

Observed
1/3 4/3 0
3 peaks

Calculated
$R = 7.75$
$S = 1.52$

Difference

Observed
5/3 2/3 0
3 peaks

Calculated
$R = 8.53$
$S = 1.40$

Difference

Fig. 6 - Observed and fitted projections onto the $\gamma$-$\omega$ plane of the groups of overlapping magnetic satellite reflections near the $-2/3$ $-2/3$ 0, $1/3$ $4/3$ 0 and $5/3$ $2/3$ 0 reciprocal lattice points of TlFeCl$_3$. 
Fig. 7 - The starting models, and the R-factors and individual integrated intensities as refinement proceeded, for three sets of poorly chosen initial parameters for the count distribution near the $1/3 4/3 0$ reciprocal lattice point of $\text{TlFeCl}_3$. The observed and final fitted distributions are shown in Fig. 6b. The matrix of first partial derivatives is calculated in cycles 1 to 16 and cycles 51 to 66.
The ellipsoidal shape parameters are constrained to be the same for all reflections within each scan. Note that the inaccuracies in the model function tend to be increasingly absorbed in the fits as the overlap of the reflections increases. This undoubtedly results in increased inaccuracy of the reduced integrated intensities. The R-factor and integrated intensities of the three individual reflections for successive cycles during the fitting of the observed distribution of Fig. 6b are shown for three different sets of starting parameters in Fig. 7. The fits converge to the same solution in all three cases, and the R-factor appears to be a good indicator of the convergence. It can also be seen that convergence may require a second calculation of the first partial derivative matrix.

Fig. 8 - 3-D fit to three overlapping magnetic reflections near the 1/3 1/3 2 reciprocal lattice point of TIPeCl₃. The γ-ω distributions in successive planes of constant v are shown.
Fig. 8 shows the 3-D fit to a group of three reflections whose centres lie in a plane at an angle to the \( y-w \) plane. Again the inaccuracies in the model function are absorbed to some extent by the number of parameters. The size of the work array required by VA05A for the 2240 observations and 20 parameters of this fit approaches the limit of our computer. For 3-D fits of larger size it would be better to replace VA05A by an algorithm that requires less storage. VA07AD could be used if the derivatives of the fitted function can be derived analytically.

For \( \omega \)-scans with a single detector, parasitic powder scattering from, for example, cryostat heat shields usually just increases the constant background observed in the 1-D profile, and thereby decreases only the precision of the reduced integrated intensity. The presence of powder scattering in 3-D distributions can significantly degrade both the precision and the accuracy of the reduced data because the scattering is localised on planes of constant \( \theta \) in the distributions. Fig. 5 shows that parasitic powder scattering can be corrected for by simultaneously fitting the single-crystal Bragg peaks by a multi-variate Gaussian, and the \( \theta \)-dependent powder scattering by a number of uni-variate Gaussians.

V - CONCLUDING REMARKS

Until now multi-dimensional diffraction data has primarily been used for:

a) quasi-simultaneous collection of several well-resolved Bragg reflections,
b) optimization of the reduced integrated intensity with respect to both accuracy and precision /13/, and
c) study of the crystal and reflection characteristics /14/.

The examples in this paper have demonstrated a further advantage, to optimize the resolution and integration of overlapping reflections. Both 2- and 3-D fits are feasible and yield reproducible results even in cases of severe overlap. For neutron reflections a multi-variate Gaussian function is often appropriate and offers considerable computational convenience.

Multi-dimensional profile fitting is not limited to multidetector data. It could be applied to any mapping of reciprocal space obtained from multiple scans with a single detector and a small aperture (see Figs. 2 and 3) provided account was taken of the step size in relation to the aperture dimensions in deriving the integrated intensities.

The use of surface plots of suitably chosen 2-D projections has proven invaluable in the development of the fitting program and analysis of the results. Because these plots display all visible counts, they can reveal details in the distribution that may not be evident in a 2-D contour plot or in display of the full 3-D array.

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