ment (for structure determination), while for some crystals with only moderate mosaic spread such data collection will be practicable.

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One-Wavelength Technique: Estimation of Centrosymmetrical Two-Phase Invariants in Dispersive Structures

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Abstract

Two-phase structure invariants of type $\Phi=\varphi_{\mathbf{h}}+\varphi_{-\mathbf{h}}$ are estimated in centrosymmetrical space groups, and in non-centrosymmetrical ones when $\varphi_{\mathbf{h}}$ is a symmetry-restricted phase. The distributions are of von Mises type with concentration parameters half those occurring in non-centric distributions.

Notation

N number of atoms in the unit cell
t number of atoms in the asymmetric unit
$f=f'+if''$ general expression for the atomic scattering factor
$F^+=A^++iB^+$, $F^-=A^-+iB^-$ structure factors of the reflexions **h** and **−h** respectively
φ^+, φ^- phases of F^+, F^-
$\mathbf{C}_S\equiv(\mathbf{R}_S,\mathbf{T}_S)$ Sth symmetry operator: $\mathbf{R}_S$ is the rotational part, $\mathbf{T}_S$ the translational part
$\xi_j=\sum_{s=1}^{m}\cos 2\pi h(\mathbf{R}_S\mathbf{r}_j+\mathbf{T}_S)$
$\eta_j=\sum_{s=1}^{m}\sin 2\pi h(\mathbf{R}_S\mathbf{r}_j+\mathbf{T}_S)$
$\varepsilon_{\mathbf{h}}$ Wilson's (1980) statistical weight of the reflection **h**
$\sum_+=\varepsilon\sum_{j=1}^{N}(f_j'^2+f_j''^2)$ average value of $|F_{\mathbf{h}}|^2$ at given $|\mathbf{h}|$
$\sum_-=\varepsilon\sum_{j=1}^{N}(f_j'^2-f_j''^2)$
$R=F/\sum_+^{1/2}$ normalized modulus of the structure factor
$D_1(x)=I_1(x)/I_0(x)$ ratio of modified Bessel functions of order 1 and 0
cs, ncs centrosymmetric, non-centrosymmetric

1. Introduction

Probabilistic approaches have been applied by several authors to crystal structures with dispersive atoms (see Srinivasan & Parthasarathy, 1976, and literature there quoted; Kroon, Spek & Krabbendam, 1977; Heinerman, Krabbendam, Kroon & Spek, 1978). Among the most recent results connected with this paper we quote:

(*a*) estimation of two-phase and three-phase structure invariants (Hauptman, 1982; Giacovazzo, 1983);

(*b*) estimation of probabilistic coefficients for a Patterson synthesis devoted to finding the positions of anomalous scatterers (Cascarano & Giacovazzo, 1984);

(*c*) formulas estimating phases of the complete crystal structures when the position of the anomalous scatterers are known (Cascarano & Giacovazzo, 1985).

Probabilistic treatment of the anomalous dispersion effect is more important in ncs space groups: accordingly all the approaches (*a*), (*b*), (*c*) were described in Cascarano & Giacovazzo (1985). It is, however, of non-negligible interest to apply probabilistic methods for the estimation of the structure invariants in cs space groups, or in ncs space groups when the invariants are constituted by symmetry-restricted phases. This paper is devoted to the estimation of two-phase structure invariants in the above conditions. For the sake of brevity we give here only the final formulas: for the mathematical approach the reader is referred to a recent book (Giacovazzo, 1980).

2. The estimation of $\Phi=\varphi_{\mathbf{h}}+\varphi_{-\mathbf{h}}$ in centrosymmetric crystals

In cs space groups $F^+\equiv F^-$: thus, in order to calculate $\Phi=\varphi_{\mathbf{h}}+\varphi_{-\mathbf{h}}$, the simpler distribution $P(A, B)$ may be calculated instead of $P(A^+, A^-, B^+, B^-)$, as has

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been done in ncs space groups (Hauptman, 1982; Giacovazzo, 1983).

The distribution $P(A, B)$ in cs crystals when dispersive atoms are present has been determined by Wilson (1980):

$$P(A, B) \simeq (2\pi\delta)^{-1} \times \exp -(\beta^2 A^2 - 2\gamma AB + \alpha^2 B^2)/(2\delta^2) \quad (1)$$

where

$$\alpha^2 = \tfrac{1}{2}(\sum_+ + \sum_-) = \varepsilon \sum_{j=1}^{N} f'^2$$

$$\beta^2 = \tfrac{1}{2}(\sum_+ - \sum_-) = \varepsilon \sum_{j=1}^{N} f''^2_j$$

$$\gamma = \varepsilon \sum_{j=1}^{N} f'_j f''_j, \qquad \delta = (\alpha^2\beta^2 - \gamma^2)^{1/2}.$$

From (1) Wilson derived the marginal distribution function

$$P(|F|) \simeq (|F|/\delta) \exp[-\textstyle\sum_+ |F|^2/(4\delta^2)] \times I_0[S|F|^2/(4\delta^2)] \quad (2)$$

where

$$S = [(\alpha^2 - \beta^2)^2 + 4\gamma^2]^{1/2}.$$

For non-zero δ the distribution (2) behaves quite differently from the distribution for a non-dispersive cs crystal and reduces to this when δ goes to zero. The conditional distribution $P(\varphi \,||F|)$ was not derived by Wilson: however, it may readily be derived by (1). We obtain

$$P(\varphi \,||F|) \simeq [2\pi I_0(Z)]^{-1} \exp[z \cos(2\varphi - \psi)] \quad (3)$$

where

$$Z = |F|^2 S/(4\delta^2) \quad (4)$$

and $\tan\psi = 2\gamma/\sum_-$.

Equation (3) is a bimodal von Mises distribution with maxima at $\varphi = \psi/2$ and $\psi/2 + \pi$. Also the distribution $P(\Phi \,||F|)$ where $\Phi = \varphi^+ + \varphi^- = 2\varphi^+$ is of interest:

$$P(\Phi \,||F|) \simeq [2\pi I_0(Z)]^{-1} \exp[Z \cos(\Phi - \psi)]. \quad (5)$$

If $|F|$ is replaced by the normalized modulus R, then (5) may be written

$$P(\Phi \mid R) \simeq [2\pi I_0(Q_c)]^{-1} \exp[Q_c \cos(\Phi - \psi)] \quad (6)$$

where $Q_c = (R^2 \sum_+ S)/(4\delta^2)$.

If (6) is compared with the distribution $P(\Phi)$ in the case of anomalous diffraction for ncs crystals [see equation (5) in Giacovazzo, 1983] it may be seen that:

(a) both cs and ncs distributions are of von Mises type;

(b) both of them reach their maximum at ψ;

(c) $Q_c = Q/2$. This result should explain why the estimation of $|F''|$ by means of equation (6) in the paper by Cascarano & Giacovazzo (1985) is more accurate in ncs space groups than in cs ones.

3. The estimation of $\Phi = \varphi_{\mathbf{h}} + \varphi_{-\mathbf{h}}$ in non-centrosymmetric crystals when Φ is a symmetry-restricted phase

In a non-dispersive structure let $\varphi_{\mathbf{h}}$ be a phase restricted (because of symmetry) to φ_r and let $\mathbf{C}_r = (\mathbf{R}_r, \mathbf{T}_r)$ be the symmetry operator for which $\mathbf{hR} = -\mathbf{h}$ (then $\varphi_r = \pi\mathbf{hT}_r + n\pi$). When dispersive atoms are present the contribution to $F_{\mathbf{h}}$ from the real part of the scattering factors will still be restricted to φ_r, while, because of the supplementary contribution from the imaginary part of the scattering factors, $\varphi_{\mathbf{h}}$ may deviate from φ_r. Since

$$F_{\mathbf{h}} = \sum_{j=1}^{t} (f'_j \xi_j - f''_j \eta_j) + i \sum_{j=1}^{t} (f'_j \eta_j + f''_j \xi_j),$$

$$F_{-\mathbf{h}} = \sum_{j=1}^{t} (f'_j \xi_j + f''_j \eta_j) + i \sum_{j=1}^{t} (-f'_j \eta_j + f''_j \xi_j),$$

$F_{\mathbf{h}}$ and $F_{-\mathbf{h}}$ are not the complex conjugates of each other but the identity $|F_{\mathbf{h}}| = |F_{-\mathbf{h}}|$ still holds. Accordingly we can limit ourselves to calculate the joint probability distribution $P(A, B)$. We obtain

$$P(A, B) \simeq (2\pi\delta')^{-1} \exp[-(\beta'^2 A^2 - 2\gamma' AB + \alpha'^2 B^2)/(2\delta'^2)] \quad (7)$$

where

$$\alpha'^2 = \tfrac{1}{2}\textstyle\sum_+ + \tfrac{1}{2}\sum_- \cos 2\pi\mathbf{hT}_r - \gamma \sin 2\pi\mathbf{hT}_r \quad (8a)$$

$$\beta'^2 = \tfrac{1}{2}\textstyle\sum_+ - \tfrac{1}{2}\sum_- \cos 2\pi\mathbf{hT}_r + \gamma \sin 2\pi\mathbf{hT}_r \quad (8b)$$

$$\gamma' = \gamma \cos 2\pi\mathbf{hT}_r + \tfrac{1}{2}\textstyle\sum_- \sin 2\pi\mathbf{hT}_r. \quad (8c)$$

From (7) the marginal distribution

$$P(|F|) \simeq (|F|/\delta') \exp[-\textstyle\sum_+ |F|^2/(4\delta'^2)] \times I_0[S'|F|^2/(4\delta'^2)] \quad (9)$$

is readily found, where

$$\delta' = (\alpha'^2\beta'^2 - \gamma'^2)^{1/2}$$

$$S' = [(\alpha'^2 - \beta'^2)^2 + 4\gamma'^2]^{1/2}.$$

From definitions (8) it may be seen that $S' \equiv S$ and $\delta' \equiv \delta$, so that (9) coincides with (2). It may be concluded that the distribution $P(|F|)$ in ncs dispersive crystals for symmetry-restricted reflexions coincides with the distribution $P(|F|)$ in cs dispersive crystals.

From (7) the conditional distribution

$$P(\varphi \,||F|) \simeq [2\pi I_0(Z)]^{-1} \exp[Z \cos(2\varphi - \psi')] \quad (10)$$

arises, where

$$\cos\psi' = (\alpha'^2 - \beta'^2)/S, \qquad \sin\psi' = 2\gamma'/S. \quad (11)$$

Equation (10) may be considered a generalization of (5): indeed, if $\pi \mathbf{hT}_r = n\pi$, then $\alpha'^2 = \alpha^2$, $\beta'^2 = \beta^2$, $\gamma'^2 = \gamma^2$.

The distribution of $\Phi = \varphi_{\mathbf{h}} + \varphi_{-\mathbf{h}}$ may be calculated by considering that $\varphi_{\mathbf{h}} + \varphi_{-\mathbf{h}} = 2(\varphi_{\mathbf{h}} - \varphi_r)$. After a straightforward change of variable (10) becomes

$$P(\Phi \,||F|) \simeq [2\pi I_0(Z)]^{-1} \times \exp[Z \cos(\Phi + 2\varphi_r - \psi')]. \quad (12)$$

By means of (11) it may be found that

$$\cos(2\varphi_r - \psi') = \sum\nolimits_-/S \quad \text{and} \quad \sin(2\varphi_r - \psi') = 2\gamma/S$$

so that

$$\tan(2\varphi_r - \psi') = \tan\psi.$$

Equation (12) is therefore identical to (5): it may be concluded that $P(\Phi \,||F|)$ is the same both for cs crystals and for restricted-phase reflexions in ncs crystals.

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Least-Squares Absolute-Structure Refinement. A Case Study of the Effect of Absorption Correction, Data Region, Stability Constant and Neglect of Light Atoms

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Abstract

X-ray diffraction intensity data measured on two four-circle diffractometers from a crystal of the compound potassium hydrogen (2*R*, 3*R*)-tartrate have been used to study the effect of absorption correction, data region, stability constant and neglect of light atoms in the atomic model on the least-squares estimate of the absolute-structure (inversion-twin) parameter *x*. It is shown that for a complete data set with Friedel pairs measured in the same plane of diffraction, an absorption correction reduced the e.s.d. of *x* without significantly altering its value. For data sets where only one member of each Friedel pair is allowed to contribute in the least-squares analysis, e.s.d.'s and deviations of *x* from its ideal value are increased compared with complete data sets containing both members of each Friedel pair. Certain aspects of combining a complete data set consisting of one asymmetric unit of reciprocal space with all-sphere measurements of absolute-structure-sensitive reflections have also been investigated. Lowering the value of the stability constant increases the e.s.d. of *x*, produces values of *x* closer to its ideal value for complete data sets and increases the variability of *x* for incomplete data sets. Neglect of hydrogen atoms from the atomic model produces a very small but quantifiable shift in the estimated value of *x*.

Introduction

In previous work (Flack, 1983; Bernardinelli & Flack, 1985) it has been shown that absolute structure may be determined very efficiently by assuming any non-centrosymmetric crystal to be an inversion twin and letting the absolute-structure (inversion-twin) parameter *x* be a variable in the least-squares refinement. Whereas a great deal is known about the bias that may be caused in least-squares-estimated atomic positional and displacement parameters due to systematic effects such as absorption, thermal diffuse scattering, extinction, scan-range truncation *etc.*, little at present is understood of the behaviour of the absolute-structure parameter. It is the intention of this paper to present results on four systematic effects; absorption,

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