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Abstract

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COMPUTATIONAL FORMULAS FOR STRUCTURE FACTORS AND THEIR DERIVATIVES IN THE CASE OF ANISOTROPIC THERMAL VIBRATIONS

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In connection with the increase in the accuracy of measurements of X-ray scattering intensities in crystals, to a large extent due to the development of diffractometric methods of measurement, the inclusion of anisotropic thermal vibrations of atoms in structural models is becoming increasingly important.

The formulas for structure factors for various Fedorov groups, given in the International Tables (^{1}), lose their validity in the present case. A general approach to the treatment of anisotropic vibrations in the presence of symmetry was outlined in (^{2}). Certain improvements of the computational formulas for structure factors and their derivatives in connection with the development of least-squares programs are contained in (^{3,4}). In the present work, formulas for structure factors and their derivatives with respect to coordinate parameters in the case of anisotropic vibrations are obtained on the basis of the approach developed in (^{5,6}).

1. The real and imaginary components of the part of the structure factor corresponding to geometrically equivalent points of a general position, in the case of anisotropic vibrations, are described in general form by the expressions

$$A = c\sum_{n=1}^{N} \exp[-(G_{nH}, H)]A_n; \qquad B = c\sum_{n=1}^{N} \exp[-(G_{nH}, H)]B_n, \tag{1}$$

where c is a constant determined by the lattice type;

$$A_n = \cos 2\pi(hx_n + ky_n + lz_n); \qquad B_n = \sin 2\pi(hx_n + ky_n + lz_n);$$

(x_n, y_n, z_n) are the coordinates of geometrically equivalent points of a general position $r_n = (x_n, y_n, z_n)$,

$$r_n = \mathfrak{S}_n r = S_n r + t_n; \qquad n = 1, 2, \dots, N; \tag{2}$$

$r = (x, y, z)$; S_n is the 3×3 “rotation”matrix of the symmetry transformation $\mathfrak{S}_n$; t_n is a translation. The value $n = 1$ corresponds to the identity transformation $r_1 = r$.

The expression entering the exponential term is equal to

$$(G_{nH}, H) = (G_{nH})^T H = A^2_{nh} + B^2_{nk} + C^2_{nl} + 2D_{nhk} + 2E_{nhl} + 2F_{nkl}. \tag{3}$$

Here $H = (h, k, l)$; G_n is the 3×3 matrix of coefficients of the quadratic form (3); the superscript T denotes the transposition operation.

By the meaning of the symmetry transformation, the values of the quadratic forms (GH, H), where $G = G_1$, and (G_{nH}, H) in any pair of symmetric directions H and $S_n^{-T} H$ must be identical. In particular, for the pair $S^T H$ and H we have

$$(GS^T H, S^T H) = (G_{nH}, H), \tag{4}$$

i.e.,

$$(G_{nH}, H) = (GH_n, H_n) = Ah_n^2 + Bk_n^2 + Cl_n^2 + 2Dh_{nk}n + 2Eh_{nl}n + 2Fk_{nl}n, \tag{5}$$

where $H_n = (h_n, k_n, l_n) = S_n^T H$. It also follows from (4) that $(G_{nH}, H) = (S_{nGS}n^T H, H)$ for arbitrary H, whence $G_n = S_{nGS}n^T$ (see (7)). The representation of the quadratic form (3) in the form (5), adopted in (^{3,4}), is preferable from the computational point of view (see also (8)).

Following (6), let us single out from the general system of symmetry transformations (2) a rhombic subgroup of transformations

$$\mathcal{E}_1, \dots, \mathcal{E}_p; \qquad \mathcal{E}_i r = E_i r + \tau_i; \qquad E_i = \begin{pmatrix} \alpha_i & 0 & 0 \\ 0 & \beta_i & 0 \\ 0 & 0 & \gamma_i \end{pmatrix}; \qquad i = 1, 2, \dots, p, \tag{6}$$

characterized by the diagonal structure of the matrices of “rotations” E_i. The transformations (6) form a normal divisor. All transformations (2) split into q classes ($q \leq 6$) of equivalent transformations differing from one another by rhombic factors (6).

We shall carry out the summation in (1) in two steps, first collecting together the terms corresponding to transformations of one class,

$$J_j\mathcal{E}_1, \dots, J_j\mathcal{E}_p,$$

then passing to another class, etc., which corresponds to the values $j = 1, 2, \dots, q$. Note that, by virtue of the property of rhombic transformations to form a normal divisor, the product $J_j\mathcal{E}_i = \mathcal{E}'_i J_j$, where $\mathcal{E}'_i = J_j\mathcal{E}_{iJ}j^{-1}$,

$$\mathcal{E}'_i r = E_i^j r + \tau_i^j; \qquad E_i^j = \begin{pmatrix} \alpha_i^j & 0 & 0 \\ 0 & \beta_i^j & 0 \\ 0 & 0 & \gamma_i^j \end{pmatrix}.$$

The transformation $\mathcal{E}'_i$ coincides with one of the rhombic transformations (6). If $J_j r = I_{jr} + \theta_j$, then for the product $\mathcal{E}'_i J_j$ we shall have $\mathcal{E}'_i J_j r = E_i^j I_j r + t_i^j$, where $t_i^j = I_j \tau_i^j + \theta_j$.

Expanding sin and cos into sums of triple products and taking into account the character of the rhombic transformations (6), expressions (1) can be represented in the form

$$A = c\sum_{j=1}^{q}\sum_{i=1}^{p} \exp[-(G_{iH}j, H_j)]A_{ij}(r_j); \qquad B = c\sum_{j=1}^{q}\sum_{i=1}^{p} \exp[-(G_{iH}j, H_j)]A_{ij}(r_j), \tag{7}$$

where

$$\begin{pmatrix} A_{ij} \\ B_{ij} \end{pmatrix} = \begin{matrix}\cos\\ \sin\end{matrix}\, 2\pi(H, t_i^j)\,(ccc - \nu_{1i}^j ssc - \nu_{2i}^j scs - \nu_{3i}^j css) \pm$$

$$\pm \begin{matrix}\sin\\ \cos\end{matrix}\, 2\pi(H, t_i^j)\,(\mu_{0i}^j sss - \mu_{1i}^j ccs - \mu_{2i}^j csc - \mu_{3i}^j scc), \tag{8}$$

where c here denotes cos, s denotes sin, the arguments of the trigonometric factors in the triple products are respectively equal to $2\pi|h|x_j$, $2\pi|k|y_j$, and $2\pi|l|z_j$, and the coefficients are equal to

$$\nu_{1i}^j = S_{hk}\alpha_i^j\beta_i^j; \qquad \nu_{2i}^j = S_{hl}\alpha_i^j\gamma_i^j; \qquad \nu_{3i}^j = S_{kl}\beta_i^j\gamma_i^j; \tag{9}$$

$$\mu_{0i}^j = S_{hkl}\alpha_i^j\beta_i^j\gamma_i^j; \qquad \mu_{1i}^j = S_l\gamma_i^j; \qquad \mu_{2i}^j = S_k\beta_i^j; \qquad \mu_{3i}^j = S_h\alpha_i^j,$$

where the symbol S_u denotes the sign of u. As is seen from (9), the coefficients in the triple products in (8) are sign factors equal to +1 or −1. The values

$$\begin{matrix}\sin\\ \cos\end{matrix} 2\pi(H, t_i^j)$$

within the settings of the crystallographic axes adopted in the tables (^{1}) can be equal only to 0, +1, or −1.

Since for a value of sin equal to 0, cos is equal to +1 or −1, and conversely, one half of the expression on the right-hand side of (8) is always cancelled. The magnitudes of the triple products remain unchanged when i is changed, requiring recalculation only when the index j is changed. The latter count is conveniently carried out according to the scheme described in (6), reducing the computations to finding the sin and cos of the simplest arguments

$$2\pi \begin{pmatrix} h\\ k\\ l \end{pmatrix} \begin{pmatrix} x\\ y\\ z \end{pmatrix}.$$

Since, when the signs of the indices h, k, and l are changed, the magnitudes of the triple products in (8) remain unchanged, the calculation of structural factors for groups of indices differing only in signs should be carried out simultaneously. We note that, within groups of independent structural factors whose indices differ only in signs, in the settings of Tables (^{1}) the quantities

$$\begin{matrix}\sin\\ \cos\end{matrix} 2\pi(H, t_i^j)$$

also remain unchanged. The quadratic form (5) is transformed as follows:

$$\begin{gathered}(GH_n, H_n) = (GE_{iH}j, E_{iH}j) = (E_{iGE_{iH}}j, H_j) \quad \text{or}\\ (GH_n, H_n) = (G_{iH}j, H_j),\end{gathered} \tag{10}$$

where

$$G_i = E_{iGE}i, \qquad H_j = I_{jH}. \tag{11}$$

In expanded form

$$(G_{iH}j, H_j) = Ah_j^2 + Bk_j^2 + Cl_j^2 + \alpha_i\beta_i 2Dh_{jk}j + \alpha_i\gamma_i 2Eh_{jl}j + \beta_i\gamma_i 2Fk_{jl}j. \tag{12}$$

In deriving (12) it has been taken into account that $\alpha_i^2 = \beta_i^2 = \gamma_i^2 = 1$. In the process of internal summation in (7), i.e., when the index is changed, the first three terms of the quadratic form (12) remain unchanged, while in the other three only the signs change.

2. Finally, let us consider the expressions for the derivatives with respect to the coordinate parameters x, y, and z. Taking into account that

$$\begin{pmatrix} A_{ij} \\ B_{ij} \end{pmatrix} = \substack{\cos \\ \sin} 2\pi(H, J_i \mathcal{G}_{ir}) = \substack{\cos \\ \sin} 2\pi(E_{iH} j, r + \varkappa_{ij}); \qquad \varkappa_{ij} = E_{iI} j^{-1} \theta_j - t_i,$$

and carrying out the differentiation, we shall have

$$\frac{\partial A_{ij}}{\partial \begin{pmatrix} x \\ y \\ z \end{pmatrix}} = -2\pi \begin{pmatrix} \alpha_i h_j \\ \beta_i k_j \\ \gamma_i l_j \end{pmatrix} B_{ij}; \qquad \frac{\partial B_{ij}}{\partial \begin{pmatrix} x \\ y \\ z \end{pmatrix}} = 2\pi \begin{pmatrix} \alpha_i h_j \\ \beta_i k_j \\ \gamma_i l_j \end{pmatrix} A_{ij}, \tag{13}$$

where $\alpha_i, \beta_i, \gamma_i$ are found from (6), and h_j, k_j, l_j from (10). Thus, for calculating the derivatives no new quantities are required besides those used in calculating the structural factors.

If in the system of rhombic transformations (6) there is a center of inversion $r' = -r + \tau_0$, then for pairs of points symmetric with respect to the center the expression (12), and consequently the exponential factors in (7), will be the same. After collecting like terms, the multipliers in the exponential general expressions are obtained as follows:

$$\begin{pmatrix} \tilde{A}_n \\ \tilde{B}_n \end{pmatrix} = \begin{pmatrix} A_n \\ B_n \end{pmatrix} [1 \mp \cos 2\pi(H, \tau_0)] + \begin{pmatrix} B_n \\ A_n \end{pmatrix} \sin 2\pi(H, \tau_0).$$

If we now exclude the center transformation from the system (6), leaving exactly one half of the transformations, then in the settings of Tables (^{1}) we shall

have the following possible cases:

$$\begin{array}{lll} \text{for } \cos 2\pi(H, \tau_0) = 1, & \widetilde{A}_n = 2A_n, & \widetilde{B}_n = 0; \\ \text{for } \cos 2\pi(H, \tau_0) = -1, & \widetilde{A}_n = 0, & \widetilde{B}_n = 2B_n; \\ \text{for } \sin 2\pi(H, \tau_0) = \pm 1, & \widetilde{A}_n = A_n \pm B_n. & \end{array}$$

If one has in mind the calculation also of the derivatives (13), then in all cases it is necessary to know both the cosine and sine components A_n and B_n. We note that $\widetilde{B}_n = \widetilde{A}_n \operatorname{tg} \pi(H, \tau_0)$—a relation that is also valid for the entire real and imaginary components of the structure factor (see (6)) in the case of a center of inversion.

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Note: Figure translations are in progress. See original paper for figures.