# EXPRESSION OF THE BASIC COMPUTATIONAL FORMULAS OF STRUCTURAL ANALYSIS OF CRYSTALS IN TERMS OF PARAMETERS OF SYMMETRY GROUPS

CRYSTALLOGRAPHY

1966

SovietRxiv

## Abstract

## Full Text

UDC 548.1+681.142.2

*CRYSTALLOGRAPHY*

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# EXPRESSION OF THE BASIC COMPUTATIONAL FORMULAS OF STRUCTURAL ANALYSIS OF CRYSTALS IN TERMS OF PARAMETERS OF SYMMETRY GROUPS

*(Presented by Academician N. V. Belov, December 3, 1965)*

In the present work, aimed mainly at setting up tables ([1]), the computational formulas for the electron density, structural factors, and derivatives of structural factors with respect to coordinate parameters are expressed through one and the same parameters of symmetry groups. As in ([2-5]), the basis of the calculations is formed by the simplest arguments

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

the maximum number of variants of formulas within a single symmetry group has been reduced from 16 to 8. This approach has been tested on programs for the electronic computer of the Institute of Crystallography of the Academy of Sciences of the USSR and partly on the programs described in ([6, 7]).

1. An arbitrary symmetry transformation $\mathcal{S}$ in a fixed system of crystallographic axes is described by the linear expression

$$\mathbf{r}' = \mathcal{S}\mathbf{r} = \mathbf{S}\mathbf{r} + \mathbf{t}, \tag{1}$$

in which $\mathbf{r} = (x, y, z)$, $\mathbf{r}' = (x', y', z')$ are the radius vectors of the initial and symmetry-related points; $\mathbf{S} = \|s_{mn}\|$ is a $3 \times 3$ rotation matrix, $\mathbf{t} = (t_1, t_2, t_3)$ is a translation. The elements $s_{mn}$ are always either 0 or $\pm 1$, and the nonzero components of $\mathbf{t}$ are fractions with denominators equal to 2, 3, 4, or 6.

We shall restrict ourselves to consideration of the factor group of symmetry transformations modulo the subgroup of translations, i.e., we shall consider all transformations up to pure translations.

From the complete system of transformations

$$\mathcal{S}_1,\ \mathcal{S}_2, \dots, \mathcal{S}_n \tag{2}$$

we shall select the transformations

$$\mathcal{E}_1, \mathcal{E}_2, \dots, \mathcal{E}_p; \quad \mathcal{E}_i\mathbf{r} = \mathbf{r}_i = \mathbf{E}_i\mathbf{r} + \vec{\tau}_i; \quad \mathbf{E}_i = \begin{pmatrix} \alpha_i & 0 & 0 \\ 0 & \beta_i & 0 \\ 0 & 0 & \gamma_i \end{pmatrix}; \quad i = 1, \dots, p, \tag{3}$$

which are characterized by a diagonal structure of the rotation matrices $\mathbf{E}_i$; we shall call them rhombic.

The rhombic transformations (3) form a subgroup with the property of a normal divisor (see ([7])). The system (2) decomposes into $q$ nonintersecting classes of equivalent transformations, consisting of transformations that differ by a rhombic multiplier. Selecting one representative from each class, we obtain the system

$$\mathcal{Y}_1, \mathcal{Y}_2, \dots, \mathcal{Y}_q; \quad \mathcal{Y}_j\mathbf{r} = \mathbf{r}_j = \mathbf{I}_j\mathbf{r} + \vec{\theta}_j; \quad j = 1, \dots, q, \tag{4}$$

of nonequivalent transformations. Note that always $p \leq 8$, $q \leq 6$. By virtue of the property of a normal divisor (see ([8])), transformation of an arbitrary rhombic transformation $\mathcal{E}_i$ with respect to the transformation $\mathcal{Y}_j$ of system (4) will again be a rhombic transformation $\mathcal{Y}_j^{-1}\mathcal{E}_i\mathcal{Y}_j = \mathcal{E}_{i'}$, generally speaking different from the original one; for the corresponding rotation matrices of these transformations we have

$$\mathbf{I}_j^{-1}\mathbf{E}_i\mathbf{I}_j = \mathbf{E}_{i'}, \tag{5}$$

in this case the matrices $E_i$ and $E_{i'}$ will differ only by a permutation of their diagonal elements, the same for all $i = 1, \dots, p$ at fixed $j$. The system of transformations (4) will correspond to the sequence of permutations

$$\pi_1, \pi_2, \dots, \pi_q \tag{6}$$

of the diagonal elements in system (3).

To the symmetry transformation (1) in reciprocal space there corresponds the relation of the structure factors: $F_{H'} = \exp[2\pi i(\mathbf{H}', \mathbf{t})]F_H^n$, where $\mathbf{H}' = S^{-T}\mathbf{H}$ (see (5)), $(\mathbf{H}', \mathbf{t}) = h't_1 + k't_2 + l't_3$, which in the particular case of rhombic transformations (3) takes the form

$$F_{H_j} = \exp[-2\pi i(\mathbf{H}, \vec{\tau}_j)]F_H; \qquad j = 1, 2, \dots, p, \tag{7}$$

where $\mathbf{H}_j = E_j\mathbf{H} = (\alpha_{jh}, \beta_{jk}, \gamma_{jl})$, $\vec{\tau}_j = (\tau_1^{(j)}, \tau_2^{(j)}, \tau_3^{(j)})$. In the case of inversion

$$\mathcal{E}\mathbf{r} = -\mathbf{r} + \vec{\tau} \tag{8}$$

provided Friedel' s law $F_{\overline{\mathbf{H}}} = F_H^*$ is satisfied, we shall have $F_H^* = \exp[-2\pi i(\mathbf{H}, \vec{\tau})]F_H^*$. Hence the phase of the structure factor $\varphi = \pi(\mathbf{H}, \vec{\tau}) + \pi m$, where $m$ is an integer (see also (10)).

Acting within the set of eight structure factors

$$F_{hkl},\ F_{\bar{h}kl},\ F_{h\bar{k}l},\ F_{hk\bar{l}},\ F_{\bar{h}\bar{k}l},\ F_{\bar{h}k\bar{l}},\ F_{h\bar{k}\bar{l}},\ F_{\bar{h}\bar{k}\bar{l}}, \tag{9}$$

each relation (7) reduces the number of independent parameters of system (9) by a factor of two. In one group there may act up to three independent relations (7); therefore, with Friedel' s law also satisfied, the number of independent parameters in (9) may decrease from 16 to one.

2. The formula for the electron density can be represented in the form

$$\rho(x,y,z) = \frac{c_1}{v}\sum_{h=0}^{\infty}\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\frac{c_2}{2^m}(\Phi_{0CCC}-\Phi_{1SSC}-\Phi_{2SCS}-\Phi_{3CSS}+\Psi_{0SSS}-\Psi_{1CCS}-\Psi_{2CSC}-\Psi_{3SCC}), \tag{10}$$

where, for brevity, $s$ and $c$ in the triple products denote sin and cos of arguments respectively equal to $2\pi hx$, $2\pi ky$, and $2\pi lz$; $m$ is the number of zeros in the triple of indices $h, k, l$. If the structure has no center of inversion, then the factor $c_1 = 2$, and the coefficients of the triple products are equal to

$$\Phi_i = \sum_H \left[\nu_i(\mathbf{H})F_H^A + \nu_i'(\mathbf{H})F_H^B\right]; \qquad \Psi_i = \sum_H \left[\mu_i(\mathbf{H})F_H^A + \mu_i'(\mathbf{H})F_H^B\right]; \tag{11}$$

in the presence of the center described by relation (8), the constant $c_1 = 1$,

$$\Phi_i = \sum_H \left[\nu_i(\mathbf{H}) + \nu_i'(\mathbf{H})\,\mathrm{tg}\,\pi(\mathbf{H}, \vec{\tau})\right] F_H^A;$$

$$\Psi_i = \sum_H \left[\mu_i(\mathbf{H}) + \mu_i'(\mathbf{H})\,\mathrm{tg}\,\pi(\mathbf{H}, \vec{\tau})\right] F_H^A \tag{12}$$

or

$$\Phi_i = \sum_H \left[\nu_i(\mathbf{H})\,\mathrm{ctg}\,\pi(\mathbf{H}, \vec{\tau}) + \nu_i'(\mathbf{H})\right] F_H^B;$$

$$\Psi_i = \sum_H \left[\mu_i(\mathbf{H}) \operatorname{ctg} \pi(\mathbf{H}, \vec{\tau}) + \mu_i'(\mathbf{H})\right] F_H^B,$$

$$i = 0, 1, 2, 3. \tag{12'}$$

The summation in the right-hand sides of (11), (12), and (12′) is carried out over the independent structure factors $F_H = F_H^A + iF_H^B$ of the set (9), taking into account the relations (7) caused by the rhombic transformations, and Friedel' s law. The quantities $\nu_i, \nu_i', \mu_i$, and $\mu_i'$ take the values $0, \pm 1$ and

$$\begin{gathered}
\begin{pmatrix} v_0 \\ v_0' \end{pmatrix} = \frac{1}{c_2} \begin{pmatrix} v_0 \\ v_0' \end{pmatrix}; \qquad \begin{pmatrix} v_1 \\ v_1' \end{pmatrix} = \frac{S_{hk}}{c_2} \begin{pmatrix} v_1 \\ v_1' \end{pmatrix}; \qquad \begin{pmatrix} v_2 \\ v_2' \end{pmatrix} = \frac{S_{hl}}{c_2} \begin{pmatrix} v_2 \\ v_2' \end{pmatrix}; \\
\begin{pmatrix} v_3 \\ v_3' \end{pmatrix} = \frac{S_{kl}}{c_2} \begin{pmatrix} v_3 \\ v_3' \end{pmatrix}; \qquad \begin{pmatrix} \mu_0 \\ \mu_0' \end{pmatrix} = \frac{S_{hkl}}{c_2} \begin{pmatrix} w_0 \\ w_0' \end{pmatrix}; \qquad \begin{pmatrix} \mu_1 \\ \mu_1' \end{pmatrix} = \frac{S_l}{c_2} \begin{pmatrix} w_1 \\ w_1' \end{pmatrix}; \\
\begin{pmatrix} \mu_2 \\ \mu_2' \end{pmatrix} = \frac{S_k}{c_2} \begin{pmatrix} w_2 \\ w_2' \end{pmatrix}; \qquad \begin{pmatrix} \mu_3 \\ \mu_3' \end{pmatrix} = \frac{S_h}{c_2} \begin{pmatrix} w_3 \\ w_3' \end{pmatrix},
\end{gathered} \tag{13}$$

where $S_u$ is a multiplier equal to $+1$ if $u \geqslant 0$, and to $-1$ otherwise;

$$\begin{gathered}
\begin{pmatrix} v_0 \\ v_0' \end{pmatrix} = \sum_i \begin{matrix}\cos \\ \sin\end{matrix} 2\pi(\mathbf{H}, \vec{\tau}_i); \qquad \begin{pmatrix} w_0 \\ w_0' \end{pmatrix} = \sum_i \alpha_i\beta_i\gamma_i \begin{matrix}\sin \\ -\cos\end{matrix} 2\pi(\mathbf{H}, \vec{\tau}_i); \\
\begin{pmatrix} v_1 \\ v_1' \end{pmatrix} = \sum_i \alpha_i\beta_i \begin{matrix}\cos \\ \sin\end{matrix} 2\pi(\mathbf{H}, \vec{\tau}_i); \qquad \begin{pmatrix} w_1 \\ w_1' \end{pmatrix} = \sum_i \gamma_i \begin{matrix}\sin \\ -\cos\end{matrix} 2\pi(\mathbf{H}, \vec{\tau}_i); \\
\begin{pmatrix} v_2 \\ v_2' \end{pmatrix} = \sum_i \alpha_i\gamma_i \begin{matrix}\cos \\ \sin\end{matrix} 2\pi(\mathbf{H}, \vec{\tau}_i); \qquad \begin{pmatrix} w_2 \\ w_2' \end{pmatrix} = \sum_i \beta_i \begin{matrix}\sin \\ -\cos\end{matrix} 2\pi(\mathbf{H}, \vec{\tau}_i); \\
\begin{pmatrix} v_3 \\ v_3' \end{pmatrix} = \sum_i \beta_i\gamma_i \begin{matrix}\cos \\ \sin\end{matrix} 2\pi(\mathbf{H}, \vec{\tau}_i); \qquad \begin{pmatrix} w_3 \\ w_3' \end{pmatrix} = \sum_i \alpha_i \begin{matrix}\sin \\ -\cos\end{matrix} (\mathbf{H}, \vec{\tau}_i);
\end{gathered} \tag{14}$$

here $\alpha_i$, $\beta_i$, $\gamma_i$ and $\vec{\tau}_i$ are the parameters of the rhombic transformations (3); the summation on the right-hand sides of (14) is from $i = 1$ to $i = p$. For the group $P1$, formulas (10)–(11) essentially coincide with those given in (11), p. 343.

As is seen from (14), the final form of the right-hand sides of formulas (11), (12), and (12′), in addition to the parameters of the rhombic transformations, will also depend on the current values of the indices $h$, $k$, and $l$; the various variants of these formulas, and consequently also formulas (10), will ultimately be determined by the residues $\gamma_1$, $\gamma_2$, and $\gamma_3$ in the right-hand sides of the system of congruences

$$\begin{aligned}\gamma_{11}h+\gamma_{12}k+\gamma_{13}l &\equiv \gamma_1 \pmod{m_1},\\ \gamma_{21}h+\gamma_{22}k+\gamma_{23}l &\equiv \gamma_2 \pmod{m_2},\\ \gamma_{31}h+\gamma_{32}k+\gamma_{33}l &\equiv \gamma_3 \pmod{m_3},\end{aligned}$$

the coefficients $\gamma_{ij}$ of whose left-hand sides are determined by the symmetry group, the setting, and, within (1), can take the values 0, $\pm1$, and $\pm2$; the moduli $m_1$, $m_2$, and $m_3$ of the congruences are equal to 0, 2, or 4. The largest number of variants within one group is not more than 8. The multiplier $c_2$ from (10), depending on the group and the variant, may be equal to 1, 2, 4, or 8. Note that in most settings (1) the values $v_i'$ and $\mu_i$, $i=0,\ 1,\ 2,\ 3$, are all equal to zero. The total number of nonzero values of the left-hand sides of (14) for all variants does not exceed 20.

3. In considering formulas for structural factors, following (1), we shall restrict ourselves to expressions for groups of geometrically equivalent points in general position. Taking into account the complete system of symmetry transformations (2) and the lattice type, these expressions may be represented in the form

$$A = c_3\sum_{j=1}^{q} a(\mathbf{r}_j); \qquad B = c_3\sum_{j=1}^{q} b(\mathbf{r}_j), \tag{15}$$

where $c_3 = c_2c_4$, with $c_2$ the same quantity as above, while $c_4$, depending on the lattice type, may be equal to 1, 2, 3, or 4; $\mathbf{r}_j$, $j=1,\ 2,\dots,\ q$, is a subsystem of points equivalent under the nonrhombic transformations (4);

$$\begin{aligned}\begin{pmatrix}a(\mathbf{r}_j)\\ b(\mathbf{r}_j)\end{pmatrix} = \begin{pmatrix}v_0\\ v_0'\end{pmatrix}ccc - \begin{pmatrix}v_1\\ v_1'\end{pmatrix}ssc - \begin{pmatrix}v_2\\ v_2'\end{pmatrix}scs - \begin{pmatrix}v_3\\ v_3'\end{pmatrix}css\\ + \begin{pmatrix}\mu_0\\ \mu_0'\end{pmatrix}sss - \begin{pmatrix}\mu_1\\ \mu_1'\end{pmatrix}ccs - \begin{pmatrix}\mu_2\\ \mu_2'\end{pmatrix}csc - \begin{pmatrix}\mu_3\\ \mu_3'\end{pmatrix}scc;\end{aligned} \tag{16}$$

here, as before, $s$ denotes sin, $c$ denotes cos, and the arguments of the triple products are respectively equal to $2\pi|h|x_j$, $2\pi|k|y_j$, and $2\pi|l|z_j$; the coefficients $\binom{\nu_i}{\nu_i'}$ and $\binom{\mu_i}{\mu_i'}$, $i=0,1,2,3$, are determined by formulas (13) and (14); note that for $j=1,2,\dots,q$ they retain constant values.

In the case of a centrosymmetric structure, the components $A$ and $B$ are connected by the additional relation $A/B = \operatorname{tg}\pi(\mathbf{H},\vec{\tau})$, where $\vec{\tau}$ is the translation participating in the inversion transformation (8); therefore, in calculating structure factors, as well as their derivatives, it is sufficient to confine oneself to the computation of one of these components by formulas (15) and (16).

Let us denote by

$$a_{\mathrm{I}},\ a_{\mathrm{II}},\ a_{\mathrm{III}};\qquad b_{\mathrm{I}},\ b_{\mathrm{II}},\ b_{\mathrm{III}} \tag{17}$$

the expressions obtained by termwise differentiation of the right-hand sides of (16), respectively with respect to the 1st, 2nd, and 3rd arguments of the trigonometric factors (which reduces to multiplying the right-hand sides of (16) by a constant factor and permuting the coefficients). Let $\vec{\pi}_j = (j_{\mathrm{I}}, j_{\mathrm{II}}, j_{\mathrm{III}})$ be a permutation of the elements I, II, III taken from system (6). Then the derivatives with respect to the coordinates $x, y, z$ of an independent atom in the $j$-th class will be equal to

$$\begin{aligned}
&\partial a(\mathbf{r}_j)/\partial x = 2\pi h_j a_{j_{\mathrm{I}}}(\mathbf{r}_j); \quad \partial b(\mathbf{r}_j)/\partial x = 2\pi h_j b_{j_{\mathrm{I}}}(\mathbf{r}_j);\\
&\partial a(\mathbf{r}_j)/\partial y = 2\pi k_j a_{j_{\mathrm{II}}}(\mathbf{r}_j); \quad \partial b(\mathbf{r}_j)/\partial y = 2\pi k_j b_{j_{\mathrm{II}}}(\mathbf{r}_j);\\
&\partial a(\mathbf{r}_j)/\partial z = 2\pi l_j a_{j_{\mathrm{III}}}(\mathbf{r}_j); \quad \partial b(\mathbf{r}_j)/\partial z = 2\pi l_j b_{j_{\mathrm{III}}}(\mathbf{r}_j);
\end{aligned} \tag{18}$$

the quantities $(h_j, k_j, l_j) = \mathbf{H}_j$ are found from the expression $\mathbf{H}_j = \mathbf{I}_j^T \mathbf{H}$, in which $\mathbf{H} = (h, k, l)$, and $\mathbf{I}_j^T$ is the transposed matrix of the $j$-th transformation of system (4). Using (15)–(18), one readily obtains the total derivatives $\partial A/\partial x$, $\partial A/\partial y$, $\partial A/\partial z$ and $\partial B/\partial x$, $\partial B/\partial y$, $\partial B/\partial z$.

The trigonometric quantities

$$\begin{matrix}\sin\\ \cos\end{matrix} 2\pi \begin{pmatrix} |h|x \\ |k|y \\ |l|z \end{pmatrix}_j ,$$

which enter into (16), as well as the expressions (17) derived from them, are computed on the basis of (4) from the initial values

$$\begin{matrix}\sin\\ \cos\end{matrix} 2\pi \begin{pmatrix} |h| \\ |k| \\ |l| \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

and the table of quantities

$$\begin{matrix}\sin\\ \cos\end{matrix} 2\pi \begin{pmatrix} |h|t_1 \\ |k|t_2 \\ |l|t_3 \end{pmatrix}_j ,$$

where $t_1^{(j)}, t_2^{(j)}, t_3^{(j)}$ are the components of the translation $\mathbf{t}_j$ of the transformation $g_j$ of system (4), $j = 1, \ldots, q$. The latter table is common to all atoms of the independent part of the unit cell; moreover, the components $t_1^{(j)}, t_2^{(j)}, t_3^{(j)}$ are always zeros or fractions with denominators equal to 2, 3, 4, or 6, and an

insignificant amount of memory is required for storing this table. The main machine time in computing the independent structure factors of each octet (9) and their derivatives will consist of the time needed to obtain the quantities

$$\begin{matrix}\sin\\ \cos\end{matrix} 2\pi \begin{pmatrix}|h|\\ |k|\\ |l|\end{pmatrix} \begin{pmatrix}x\\ y\\ z\end{pmatrix}$$

for the atoms of the independent part of the cell. It is therefore expedient to provide for the preliminary generation of the program for calculating the required part of these quantities, depending on the specific values of the parameters of the system of rotation matrices $\mathbf{I}_j$ of the non-origin-shift transformations (4) (see (7)).

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Received
7 V 1965

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