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The Calculation of Structure Factors for Centrosymmetric Monoclinic Systems with Anisotropic Atomic Vibration*

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The structure-factor expressions for centrosymmetric monoclinic space groups, with anisotropic thermal vibration, are derived and listed. They are shown to be similar to those for isotropic vibration save for correction terms which arise because symmetry-related atoms are not oriented parallel to one another. The expressions for general (*hkl*) structure factors are given first and then simpler forms for two-dimensional analyses are derived. The constants of the ellipsoid of vibration are related to parameters appropriate for least-squares refinement. Finally, extensions to some other symmetries are discussed.

1. Introduction and notation

As more powerful computing aids become available, the accuracy with which crystal-structure analysis can be carried out will depend to an increasing extent on the correct choice of atomic scattering factor curves and thermal vibration parameters. Cochran (1951*b*) has described methods of obtaining vibration parameters from (F_o-F_c) syntheses, and this paper deals with expressions for computing structure factors from known parameters.

Structures having point-group symmetry $2/m$ contain centrosymmetrical pairs of effectively anisotropic atoms which must have the same anisotropic scattering factor for all reflexion planes. Atoms related by the axis or plane, however, are not oriented parallel to one another and may have differing scattering factors for planes which are neither parallel nor perpendicular to the twofold axis. Every other point group, similarly, gives rise to its own set of related orientations and so to a set of atomic scattering factor expressions applying to all the derivative space groups.

Two procedures can be adopted for the calculation of structure factors. One is to compute the contribution of each atom associated with a lattice point (or of half of these atoms if there is a centre of symmetry). The other is to compute two separate terms, if the symmetry is monoclinic, for each atom of the asymmetric unit.

The second method involves only half the numerical work needed for the first if a set of structure factors exists which has to be corrected only for misalignment of the atomic anisotropy relative to the symmetry elements. When it is necessary to calculate an entirely new set of structure factors, however, each method requires about the same labour. The choice of procedure will then depend on the particular computing facilities available.

The expressions for general (*hkl*) structure factors are given first, because the corrections are expected to be of most use in precision analyses, which are commonly carried out by three-dimensional methods.

The notation of *International Tables for X-ray Crystallography* (1952) is used. Quantities not defined therein are:

x^*, y^*, z^*: coordinates of a reciprocal point, referred to orthogonal axes, in units of $(2 \sin \theta/\lambda)$.
q_i: thermal vibration parameters in stated directions i.
g_{ik}: direction cosines of i relative to k.
$\sum_r$: summation over the atoms r of the asymmetric unit.
$\alpha, \beta, \gamma, \delta, \varepsilon, \eta$: vibration parameters appropriate for least-squares refinement.

2. General (*hkl*) structure factors

The scattering factor for symmetry related atoms

The scattering factor of an atom will be discussed in terms of its ellipsoid of vibration, which is taken to be an ellipsoid in reciprocal space on which the temperature factor is constant.

The scattering factors for a single set of atoms in general equivalent positions will be considered. Let an atom of this set have temperature factor:

$$T = \exp\left[-\sum_i q_i h_i^2\right],$$

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where $i = 1, 2, 3$, for each of the three principal axes of the ellipsoid of vibration, and h_i is the component of $(2 \sin\theta/\lambda)$ in the direction i.

Let the direction cosines of these principal axes with respect to **a***, **b*** and **c*** be respectively g_{i1}, g_{i2} and g_{i3}.

Then, if the scattering factor for the atom at rest be f_0, that for the vibrating atom is

$$f_1 = f_0 \exp\left[\sum_i -q_i(hg_{i1}a^*+kg_{i2}b^*+lg_{i3}c^*)^2\right]. \quad (1)$$

For the atom related by the symmetry centre the scattering factor is identical, but for the pair related to these two by the plane of symmetry the direction cosines are g_{i1}, $-g_{i2}$ and g_{i3} so that the scattering factor for these two atoms is

$$f_2 = f_0 \exp\left[\sum_i -q_i(hg_{i1}a^*-kg_{i2}b^*+lg_{i3}c^*)^2\right]. \quad (2)$$

These reduce to

$$f_1 = f_0 \exp\left[\sum_i -q_i\{(hg_{i1}a^*+lg_{i3}c^*)^2+kg_{i2}b^*)^2\}\right] \times \exp\left[\sum_i -2q_i(hg_{i1}a^*+lg_{i3}c^*)kg_{i2}b^*\right]$$

and

$$f_2 = f_0 \exp\left[\sum_i -q_i\{(hg_{i1}a^*+lg_{i3}c^*)^2+(kg_{i2}b^*)^2\}\right] \times \exp\left[\sum_i +2q_i(hg_{i1}a^*+lg_{i3}c^*)kg_{i2}b^*\right].$$

We now define two new quantities:

$$\Delta f = \tfrac{1}{2}(f_1-f_2) = f_0 \exp\left[\sum_i -q_i\{(hg_{i1}a^*+lg_{i3}c^*)^2+(kg_{i2}b^*)^2\}\right] \times \sinh\left[-\left\{\sum_i 2q_i(hg_{i1}a^*+lg_{i3}c^*)kg_{i2}b^*\right\}\right]$$

and

$$\bar{f} = \tfrac{1}{2}(f_1+f_2) = f_0 \exp\left[\sum_i -q_i\{(hg_{i1}a^*+lg_{i3}c^*)^2+(kg_{i2}b^*)^2\}\right] \times \cosh\left[-\left\{\sum_i 2q_i(hg_{i1}a^*+lg_{i3}c^*)kg_{i2}b^*\right\}\right], \quad (3)$$

so that

$$\Delta f = \bar{f}\tanh\left[-\left\{\sum_i 2q_i(hg_{i1}a^*+lg_{i3}c^*)kg_{i2}b^*\right\}\right]. \quad (4)$$

$\bar{f}$ is used in the calculation of F in place of the isotropic f as coefficient of the same trigonometric term. The correction term contains Δf, which may be computed more quickly from $\bar{f}$ by (4) than directly from f_0.

Where the anisotropy is small, or the principal axes of the vibration ellipsoids are nearly parallel to the symmetry elements, the cosh term in (3) may be neglected and the tanh in (4) replaced by a sinh.

Parameters appropriate for least-squares refinement

By least-squares analysis it is possible to determine the scattering factor of an atom in the form

$$f = f_0 \exp\left[-(h^2\alpha+k^2\beta+l^2\gamma+hk\delta+kl\varepsilon+hl\eta)\right].$$

The coefficients $\alpha, \ldots, \eta$ may be expressed in terms of the constants of the vibration ellipsoid explicitly:

$$\left.\begin{aligned} \alpha &= \sum_i q_i g_{i1}^2 a^{*2}, & \delta &= \sum_i 2q_i g_{i1}g_{i2}a^*b^*, \\ \beta &= \sum_i q_i g_{i2}^2 b^{*2}, & \varepsilon &= \sum_i 2q_i g_{i2}g_{i3}b^*c^*, \\ \gamma &= \sum_i q_i g_{i3}^2 c^{*2}, & \eta &= \sum_i 2q_i g_{i3}g_{i1}c^*a^*. \end{aligned}\right\} \quad (5)$$

To obtain the constants of the ellipsoid from $\alpha, \ldots, \eta$ it is convenient to use an orthogonal set of reciprocal axes, two of these being coincident with **a*** and **b***. Consequently:

$$\left.\begin{aligned} x^* &= ha^*+lc^*\cos\beta^*, \\ y^* &= kb^*, \\ z^* &= lc^*\sin\beta^*. \end{aligned}\right\} \quad (6)$$

Writing

$$-\ln T = (\alpha h^2, \ldots, \eta hl) = (\alpha' x^{*2}, \ldots, \eta' x^*z^*),$$

we have

$$\left.\begin{aligned} \alpha' &= (\alpha/a^{*2}), \\ \beta' &= (\beta/b^{*2}), \\ \gamma' &= (\gamma/c^{*2}\sin^2\beta^* - \eta/a^*c^*\sin\beta^*\tan\beta^* + \alpha/a^{*2}\tan^2\beta^*), \\ \delta' &= (\delta/a^*b^*), \\ \varepsilon' &= (\varepsilon/b^*c^*\sin\beta^* - \delta/a^*b^*\tan\beta^*), \\ \eta' &= (\eta/a^*c^*\sin\beta^* - 2\alpha/a^{*2}\tan\beta^*). \end{aligned}\right\} \quad (7)$$

For the principal vibration directions only, the surface of the vibration ellipsoid is normal to the radius vector. Expressing this for a principal direction of parameter q_i and direction cosines $g'_{i1}, g'_{i2}, g'_{i3}$ relative to the orthogonal axes, we have three equations:

$$\partial(-\ln T)/\partial x^* = \text{grad}\,(-\ln T).g'_{i1}, \text{ etc.}$$

These may be re-written

$$\left.\begin{aligned} 2(\alpha'-q_i)g'_{i1}+\delta' g'_{i2}+\eta' g'_{i3} &= 0, \\ \delta' g'_{i1}+2(\beta'-q_i)g'_{i2}+\varepsilon' g'_{i3} &= 0, \\ \eta' g'_{i1}+\varepsilon' g'_{i2}+2(\gamma'-q_i)g'_{i3} &= 0. \end{aligned}\right\} \quad (8)$$

Solutions for g'_{i1}/g'_{i2} and g'_{i1}/g'_{i3} do not exist except for the three values of q_i satisfying the cubic equation

$$\begin{vmatrix} 2(\alpha'-q) & \delta' & \eta' \\ \delta' & 2(\beta'-q) & \varepsilon' \\ \eta' & \varepsilon' & 2(\gamma'-q) \end{vmatrix} = 0.$$

For each of these q_i, equations (8) are used to find the ratios of the g'_{ik} and thence the actual g'_{ik}, since $\sum_k g'^2_{ik} = 1$. Finally the g_{ik} are obtained from

$$\begin{aligned} g_{i1} &= g'_{i1}, \\ g_{i2} &= g'_{i2}, \\ g_{i3} &= g'_{i3}\sin\beta^* + g'_{i1}\cos\beta^*, \end{aligned}$$

An example of the use of this method is given by Davies & Blum (1955).

The structure factor for the unit cell

The expression for the structure factor for the unit cell is different from one space group to another. For brevity the results for space groups other than $P2_1/c$ will merely be quoted.

For the space group $P2_1/c$ the general equivalent positions are

$$\pm(x, y, z),\ \pm(x, \tfrac{1}{2}-y, \tfrac{1}{2}+z)\ .$$

Therefore

$$F = 2\sum_r f_{1r}\cos 2\pi(hx_r+ky_r+lz_r) + f_{2r}\cos 2\pi(hx_r-ky_r+lz_r+\tfrac{1}{2}(k+l))\ .$$

This reduces to

$$F = 4\sum_r \bar{f}_r\cos 2\pi(hx_r+lz_r).\cos 2\pi ky_r - 4\sum_r \Delta f_r \sin 2\pi(hx_r+lz_r).\sin 2\pi ky_r \quad (9)$$

for $(k+l)$ even, or to

$$F = -4\sum_r \bar{f}_r \sin 2\pi(hx_r+lz_r).\sin 2\pi ky_r + 4\sum_r \Delta f_r \cos 2\pi(hx_r+lz_r).\cos 2\pi ky_r \quad (10)$$

for $(k+l)$ odd.

Table 1. *Structure-factor expressions for monoclinic space groups*

Space group	Group of planes	Expression
$P2/m$	All planes	9
$P2_1/m$	k even	9
	k odd	10
$C2/m$	$h+k$ even	9*
	$h+k$ odd	$F = 0$
$P2/c$	l even	9
	l odd	10
$P2_1/c$	$k+l$ even	9
	$k+l$ odd	10
$C2/c$	$h+k$ even, l even	9*
	$h+k$ even, l odd	10*
	$h+k$ odd	$F = 0$

* For these space groups the factors 4 in the equations must be replaced by 8 because there are eight instead of four general equivalent positions.

The quantities $\bar{f}$ and Δf are given by equations (3) and (4).

The results for all the centrosymmetrical monoclinic space groups are given in Table 1.

3. Forms for two-dimensional analyses

The **b** *projection*

When $k = 0$, $\Delta f = 0$ (by equation (4)), and, by equation (3),

$$\bar{f} = f_0 \exp\left[\sum_i -q_i(hg_{i1}a^*+lg_{i3}c^*)^2\right].$$

This simplification expresses the fact that the projections of the ellipsoids of vibration for symmetry-related atoms on the plane normal to **b** are all parallel. An example of the use of this type of expression is given by Cochran (1951*a*).

The **c** *and* **a** *projections*

When $l = 0$

$$\bar{f} = f_0 \exp\left[h^2a^{*2}\left(\sum_i -q_ig_{i1}^2\right)+k^2b^{*2}\left(\sum_i -q_ig_{i2}^2\right)\right] \times \cosh\left[-\{hka^*b^*\left(\sum_i 2q_ig_{i1}g_{i2}\right)\}\right] \quad (11)$$

and

$$\Delta f = \bar{f}\tanh\left[-\{hka^*b^*\left(\sum_i 2q_ig_{i1}g_{i2}\right)\}\right]. \quad (12)$$

In general, in a two-dimensional analysis, the vibrational parameters are determined from an (F_o-F_c) synthesis of the projection. This gives, not the q_i and their direction cosines, but the constants of the ellipse representing the components of vibration of the atoms normal to the projection axis. (This is a general section of the ellipsoid of vibration.) Let the constants of this ellipse be q_1 and q_2 with direction cosines relative to **a*** and **b*** respectively:

$$\text{for } q_1\text{: } g_{11}, g_{12};\quad \text{for } q_2\text{: } g_{12}, -g_{11}\ .$$

Equations (11) and (12) then become

$$\bar{f} = f_0 \exp\left[-\{h^2a^{*2}(q_1g_{11}^2+q_2g_{12}^2)+k^2b^{*2}(q_1g_{12}^2+q_2g_{11}^2)\}\right] \times \cosh\left[-hka^*b^*2(q_1-q_2)g_{11}g_{12}\right] \quad (13)$$

and

$$\Delta f = \bar{f}\tanh\left[-hka^*b^*2(q_1-q_2)g_{11}g_{12}\right]. \quad (14)$$

It can be seen that the calculation takes the same form as for a system in which the principal vibration directions of the atoms are parallel to **a*** and **b***, except for the correction terms involving the cosh and tanh functions, which grow in importance as the product hk increases. Thus the effect of non-parallel vibration ellipsoids is important for reciprocal points which are far from either axis. Again, when the anisotropy is small or nearly aligned with the axes, it is a good approximation to neglect the cosh term, which is nearly unity, and to replace the tanh by a sinh. This approximation was used in the example quoted below in which the cosh term was never greater than 1·11, which corresponds to a sinh value of 0·47.

The structure-factor expressions for $P2_1/c$ (equations (9) and (10)) become

$$F = 4\sum_r \bar{f}_r\cos 2\pi hx_r.\cos 2\pi ky_r - 4\sum_r \Delta f_r \sin 2\pi hx_r.\sin 2\pi ky_r$$

for k even, and

$$F = -4\sum_r \bar{f}_r\sin 2\pi hx_r.\sin 2\pi ky_r + 4\sum_r \Delta f_r \cos 2\pi hx_r.\cos 2\pi ky_r$$

for k odd, with similar forms for other projections and space groups.

The equations take a very similar form for the **c** projection in the space group *Pnnm*, and an example of their use will be given elsewhere by Rollett.

4. Extensions to other symmetries

For the point group $\bar{1}$, the asymmetric unit occupies one-half of the unit cell. There are, therefore, no expressions allowing calculation of structure factors by summations over the atoms contained in a smaller volume. The structure factors are given by

$$F = \sum_r f_r \cos 2\pi(hx_r+ky_r+lz_r) .$$

No terms involving Δf occur because all atoms related by symmetry are oriented parallel to one another.

The orthorhombic point group *mmm* gives rise to space groups in which four different orientations are related by symmetry. The direction cosines for these are:

1.	g_{i1},	g_{i2},	g_{i3}
2.	$-g_{i1}$,	g_{i2},	g_{i3}
3.	g_{i1},	$-g_{i2}$,	g_{i3}
4.	g_{i1},	g_{i2},	$-g_{i3}$

To each set there corresponds its own scattering factor of the form of equation (1). If these are written f_1, f_2, f_3 and f_4, the structure-factor expression contains the term $(f_1+f_2+f_3+f_4)$ multiplied by the same trigonometric function as that appearing in the expression for isotropic vibration. There are also terms in which two of f_2, f_3 and f_4 are negative, and the trigonometric terms may differ by replacement of cos by sin and vice versa. Thus for *Pbca*, $(h+k)$ even and $(k+l)$ even, we have

$$\begin{aligned} F = \sum_r & 2(f_{1r}+f_{2r}+f_{3r}+f_{4r}) \cos 2\pi hx_r . \cos 2\pi ky_r . \cos 2\pi lz_r \\ & -2(f_{1r}+f_{2r}-f_{3r}-f_{4r}) \cos 2\pi hx_r . \sin 2\pi ky_r . \sin 2\pi lz_r \\ & -2(f_{1r}-f_{2r}+f_{3r}-f_{4r}) \sin 2\pi hx_r . \cos 2\pi ky_r . \sin 2\pi lz_r \\ & -2(f_{1r}-f_{2r}-f_{3r}+f_{4r}) \sin 2\pi hx_r . \sin 2\pi ky_r . \cos 2\pi lz_r . \end{aligned}$$

In general the term involving $(f_1+f_2+f_3+f_4)$ will be the most important and the others will be small corrections. Since $f_1(hkl) = f_2(\bar{h}kl)$ etc., it is sufficient to calculate f_1 for four octants to determine all the terms in the brackets.

When the anisotropies are small, or aligned nearly parallel to the axes, approximate expressions similar to those for the monoclinic case may be used to shorten the computation. These expressions are

$$f_1+f_2+f_3+f_4 = 4f_0 \exp\left[-(q_x h^2a^{*2}+q_y k^2b^{*2}+q_z l^2c^{*2})\right] ,$$

and three equations of the form

$$\frac{f_1+f_2-f_3-f_4}{f_1+f_2+f_3+f_4} = \tanh\left[-klb^*c^*\left(\sum_i 2q_i g_{i2} g_{i3}\right)\right] ,$$

where

$$q_x = \sum_i q_i g_{i1}^2, \quad q_y = \sum_i q_i g_{i2}^2, \quad q_z = \sum_i q_i g_{i3}^2 .$$

The non-centrosymmetric monoclinic point group 2 gives the same orientations as $2/m$. In consequence the structure-factor expressions for derived space groups are also similar. For $P2_1$, k even, we have

$$\begin{aligned} A = {} & 2\sum_r \bar{f}_r \cos 2\pi(hx_r+lz_r) . \cos 2\pi ky_r \\ & -2\sum_r \Delta f_r \sin 2\pi(hx_r+lz_r) . \sin 2\pi ky_r , \\ B = {} & 2\sum_r \bar{f}_r \cos 2\pi(hx_r+lz_r) . \sin 2\pi ky_r \\ & -2\sum_r \Delta f_r \sin 2\pi(hx_r+lz_r) . \cos 2\pi ky_r . \end{aligned}$$

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