Acta Cryst. (1948) **1**, 70

Phases of Fourier Coefficients directly from Crystal Diffraction Data

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(*Received* 1 *November* 1947)

It is shown that the application of Schwarz's and Cauchy's Inequalities to the formulas for calculating F_{hkl} from, respectively, the density of scattering matter and the atomic positions in a crystal leads to relations between the magnitudes of some F_{hkl}'s and the signs or phases of others. These relations are in the form of inequalities, which vary with the symmetry of the crystal under consideration. A table of the simplest inequalities applicable to crystals possessing each of the simple symmetry elements is included. Examples of the inequalities arising from the presence of combinations of symmetry elements are presented.

Introduction

The density, $\rho(x, y, z)$, of scattering matter in a crystal can be expressed as the Fourier series

$$\rho(x, y, z) = (1/V) \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F_{hkl} e^{2\pi i(hx+ky+lz)}, \quad (1)$$

where x, y and z are the 'trimetric' co-ordinates of a point in the crystal, V is the volume of a unit cell of the crystal, and h, k and l are integers. In all but very special cases $\rho(x, y, z)$ is real and therefore F_{hkl} is equal to the complex conjugate of $F_{\bar{h}\bar{k}\bar{l}}$, i.e. $F_{\bar{h}\bar{k}\bar{l}} = F^*_{hkl}$. The values of F_{hkl} can be calculated from $\rho(x, y, z)$, in the usual way, from the formula:

$$F_{hkl} = V \int_0^1 \int_0^1 \int_0^1 \rho(x, y, z) e^{-2\pi i(hx+ky+lz)} dx\,dy\,dz. \quad (2)$$

Bragg (1929) has shown that the F_{hkl}'s are related to the intensities, I_{hkl}, of X-rays diffracted by a crystal, according to the relation

$$I_{hkl} = \Phi(\lambda, \theta) |F_{hkl}|^2, \quad (3)$$

where the integers h, k and l are now the Miller indices of the crystal plane from which the diffracted beam can be said to have been 'reflected', θ is the glancing angle of reflexion (Bragg angle), λ is the wave-length of the radiation being diffracted, and $\Phi(\lambda, \theta)$ is a function, the form of which depends on the experimental arrangements.

Although other radiations can be treated by similar mathematical methods, it will always be assumed in this paper that X-radiation is used. $\rho(x, y, z)$ then represents electron density (to a very close approximation), and the units of F_{hkl} are electrons per unit cell. It is essential to the success of the following treatment that the experimentally measured values of $(I_{hkl})^{\frac{1}{2}}$ be converted to this absolute electron scale by the use of a properly chosen $\Phi(\lambda, \theta)$.

The Fourier coefficient F_{hkl} can be expressed thus

$$F_{hkl} = e^{-2\pi i \alpha_{hkl}} |F_{hkl}|,$$

where α_{hkl} is the 'phase' of F_{hkl} expressed in revolutions. The phase α_{hkl} cannot be found from the single experimental number I_{hkl}, but $|F_{hkl}|$ can. However, it will be shown that α_{hkl} can often be limited to a narrow range of values—or even determined exactly—by relations between I_{hkl} and other intensities, $I_{h'k'l'}$. The determination of α_{hkl} is the subject of this paper.

The use of Schwarz's Inequality

The relation

$$\left| \int f g d\tau \right|^2 \leqslant \left(\int |f|^2 d\tau \right) \left(\int |g|^2 d\tau \right) \quad (4)$$

is known as Schwarz's Inequality. Applying this to (2) one obtains

$$|F_{hkl}|^2 \leqslant V^2 \left[\int_0^1 \int_0^1 \int_0^1 \rho(x, y, z)\, dx\,dy\,dz \right] \times \left[\int_0^1 \int_0^1 \int_0^1 \rho(x, y, z) \left| e^{-2\pi i(hx+ky+lz)} \right|^2 dx\,dy\,dz \right]$$

or

$$|F_{hkl}|^2 \leqslant V^2 \left[\int_0^1 \int_0^1 \int_0^1 \rho(x, y, z)\, dx\,dy\,dz \right]^2.$$

Since $V dx\,dy\,dz$ is the volume element belonging to the trimetric co-ordinates x, y, z, this formula can be rewritten

$$|F_{hkl}|^2 \leqslant Z^2, \quad (5)$$

where Z is the total amount of scattering material, i.e. the total number of electrons, in the unit cell. In particular, directly from (2),

$$F_{000} = Z. \quad (6)$$

The effect of symmetry

In case the crystal contains symmetry operations, the application of Schwarz's Inequality to formula (2) provides some information regarding the phases of some of the F_{hkl}'s. For example, suppose the crystal to contain a center of inversion, $\bar{1}$, at (0, 0, 0). Then

$$\rho(x, y, z) = \rho(-x, -y, -z),$$

F_{hkl} is real and (2) can be written:

$$F_{hkl} = V \int_0^1 \int_0^1 \int_0^1 \rho(x, y, z) \cos 2\pi(hx+ky+lz)\, dx\,dy\,dz.$$

Then, by Schwarz's Inequality,

$$F_{hkl}^2 \leqslant V^2\left[\int_0^1\int_0^1\int_0^1 \rho(x,y,z)\,dx\,dy\,dz\right]$$

$$\times\int_0^1\int_0^1\int_0^1 \tfrac{1}{2}\rho(x,y,z)\,[1+\cos 2\pi(2hx+2ky+2lz)]\,dx\,dy\,dz$$

or
$$F_{hkl}^2 \leqslant Z(\tfrac{1}{2}Z+\tfrac{1}{2}F_{2h,2k,2l}). \tag{7}$$

If we define $F_{hkl}/Z=\hat{F}_{hkl}$ as the 'unitary crystal structure factor', (7) can be rewritten

$$\hat{F}_{hkl}^2 \leqslant \tfrac{1}{2}+\tfrac{1}{2}\hat{F}_{2h,2k,2l}. \tag{8}$$

This inequality is of use in finding the signs of some $F_{2h,2k,2l}$'s. Thus, if $\hat{F}_{hkl}^2$ is greater than $\frac{1}{2}$, $\hat{F}_{2h,2k,2l}$ must be positive; or, if $|\hat{F}_{2h,2k,2l}|$ is $\frac{1}{2}$ and $\hat{F}_{hkl}^2$ is larger than $\frac{1}{4}$, then $\hat{F}_{2h,2k,2l}$ is positive, and so on.

As a second example, suppose the crystal contains a two-fold rotational axis of symmetry, 2, along the y axis. In this case $\rho(x,y,z)=\rho(-x,y,-z)$ and

$$F_{hkl}=V\int_0^1\int_0^1\int_0^1 \rho(x,y,z)\,e^{-2\pi iky}\cos 2\pi(hx+lz)\,dx\,dy\,dz.$$

The application of relation (4) then leads to

$$|\hat{F}_{hkl}|^2 \leqslant \tfrac{1}{2}+\tfrac{1}{2}\hat{F}_{2h,0,2l}. \tag{9}$$

This relation is somewhat more powerful than (8), since all the observed $|F_{hkl}|^2$'s of constant h and l but various k's can be used to determine the sign of $F_{2h,0,2l}$. (In this case F_{h0l} is a real number.)

Other symmetry elements yield other inequalities by the use of very similar methods. In each case the integrand in (2) is simplified by the use of the symmetry element under discussion and Schwarz's Inequality applied. Table 1 lists the inequalities which arise from the presence of each of the simple symmetry elements.

It is to be noted that so far only the presence of glide planes or screw axes leads to inequalities that can prove the sign of an F to be negative. This situation is not as serious as might appear—the 'relations limiting the phases of odd orders' (to be discussed later) can also be used to prove signs of F's to be negative, even if no glide planes or screw axes are present.

The effect of atomic shape

Crystals are composed of atoms whose electron clouds provide the scattering matter, the density of which is given by equation (1). It is well known that if the electron clouds of the atoms are assumed spherical, equation (2) can be rewritten

$$F_{hkl}=\sum_{j=1}^{N} f_j e^{-2\pi i(hx_j+ky_j+lz_j)}, \tag{10}$$

where N is the total number of atoms in the unit cell, x_j, y_j, z_j are the (trimetric) co-ordinates of the center of the jth atom, and f_j—the 'atomic structure factor' of the jth atom—is given by

$$f_j=V\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\rho_j(x,y,z)\,e^{-2\pi i(hx+ky+lz)}\,dx\,dy\,dz,$$

where $\rho_j(x,y,z)$ is the electron density of the jth atom referred to an origin at its center. It appears that f_j depends on h, k and l, but actually this dependence is such that f_j is a function of $(\sin\theta)/\lambda$ only. Fig. 1 shows the dependence of f_j/Z_j on $(\sin\theta)/\lambda$, where Z_j is the atomic number, or number of electrons, of the jth atom. It is seen that (except for hydrogen with $Z_j=1$) the curves in Fig. 1 all lie fairly close together—at least to the accuracy with which the intensities of diffracted X-ray beams are usually measured. This suggests that the approximation $Z_j\hat{f}=f_j$ might be useful. $\hat{f}$ is then the same function of $(\sin\theta)/\lambda$ for every atom in the crystal and will be called 'the unitary atomic structure factor'.

Since
$$\sum_{j=1}^{N} Z_j=Z,$$

one obtains
$$\sum_{j=1}^{N} f_j=\hat{f}Z$$

or
$$\hat{f}=(1/Z)\sum_{j=1}^{N} f_j. \tag{11}$$

From this relation $\hat{f}$ can be calculated, as a function of $(\sin\theta)/\lambda$, for any crystal of interest. With this assumption, one can write

$$F_{hkl}=\hat{f}\sum_{j=1}^{N} Z_j e^{-2\pi i(hx_j+ky_j+lz_j)},$$

or, defining
$${}^{A}\hat{F}_{hkl}=F_{hkl}/Z\hat{f}, \tag{12}$$

where ${}^{A}\hat{F}_{hkl}$ is a 'unitary crystal structure factor assuming atoms', and

$$Z_j/Z=n_j, \tag{13}$$

where n_j is the fraction of the electrons in the unit cell on the jth atom, one can write

$${}^{A}\hat{F}_{hkl}=\sum_{j=1}^{N} n_j e^{-2\pi i(hx_j+ky_j+lz_j)}. \tag{14}$$

Cauchy's Inequality states that

$$\left|\sum_{j=1}^{N} a_j b_j\right|^2 \leqslant \left(\sum_{j=1}^{N}|a_j|^2\right)\left(\sum_{j=1}^{N}|b_j|^2\right), \tag{15}$$

where the a_j's and b_j's are any real or complex numbers; it is the stem from which Schwarz's Inequality arose. Applying (15) to (14) one obtains

$$|{}^{A}\hat{F}_{hkl}|^2 \leqslant \left(\sum_{j=1}^{N} n_j\right)\left(\sum_{j=1}^{N} n_j|\,e^{-2\pi i(hx_j+ky_j+lz_j)}\,|^2\right)$$

or, by noting that $\sum_{j=1}^{N} n_j=1$,

$$|{}^{A}F_{hkl}|^2 \leqslant 1. \tag{16}$$

This is the exact analogue of the first relation in Table 1.

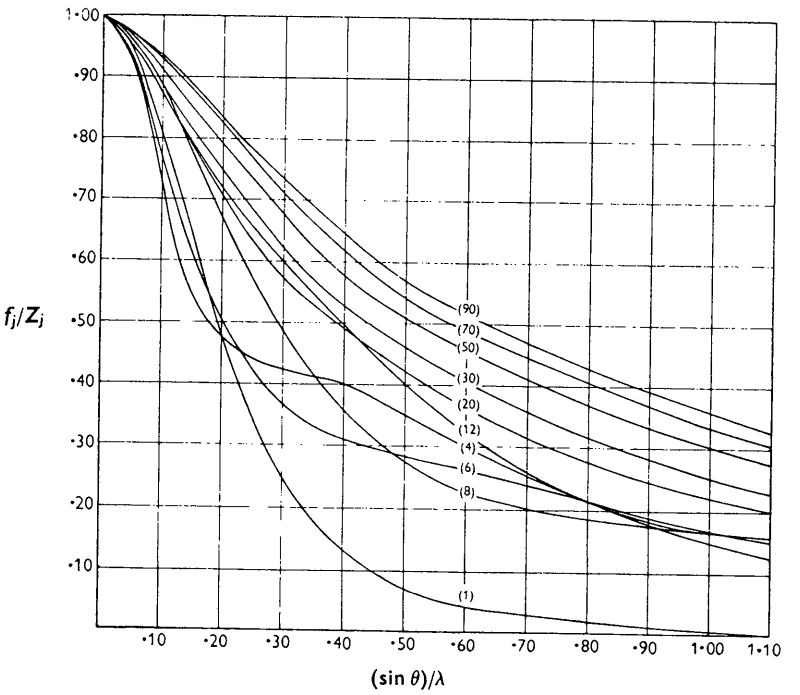

Fig. 1. Curves of f_j/Z_j as functions of (sin θ)/λ. The numbers in parentheses are the values of the atomic number, Z_j.

Table 1. *The inequalities arising from the various elements of symmetry*

(All symmetry elements pass through the origin.)

Symbol of axis	Equivalent symbol	Co-ordinates	Inequality
1	—	Triclinic	$\mid \hat{F}_{hkl} \mid^2 \leqslant 1$
$\bar{1}$	—	Triclinic	$\hat{F}^2_{hkl} \leqslant \frac{1}{2} + \frac{1}{2}\hat{F}_{2h,\,2k,\,2l}$
2	—	Monoclinic	$\mid \hat{F}_{hkl} \mid^2 \leqslant \frac{1}{2} + \frac{1}{2}\hat{F}_{2h,\,0,\,2l}$
$\bar{2}$	m	Monoclinic	$\mid \hat{F}_{hkl} \mid^2 \leqslant \frac{1}{2} + \frac{1}{2}\hat{F}_{0,\,2k,\,0}$
2_1	—	Monoclinic	$\mid \hat{F}_{hkl} \mid^2 \leqslant \frac{1}{2} + \frac{1}{2}(-1)^k \hat{F}_{2h,\,0,\,2l}$
3	—	Hexagonal	$\mid \hat{F}_{HK*L} \mid^2 \leqslant \frac{1}{3} + \frac{2}{3} \mid \hat{F}_{H-K,\,H+2K,\,*,\,0} \mid \cos 2\pi\alpha_{H-K,\,H+2K,\,*,\,0}$
$\bar{3}$	$3+\bar{1}$	Hexagonal	$\hat{F}^2_{HK*L} \leqslant \frac{1}{6} + \frac{1}{6}\hat{F}_{2H,\,2K,\,*,\,2L} + \frac{1}{3}\hat{F}_{H,\,K,\,*,\,2L} + \frac{1}{3}\hat{F}_{H-K,\,H+2K,\,*,\,0}$
3_1	—	Hexagonal	$\mid \hat{F}_{HK*L} \mid^2 \leqslant \frac{1}{3} + \frac{2}{3} \mid \hat{F}_{H-K,\,H+2K,\,*,\,0} \mid \cos 2\pi\,(\alpha_{H-K,\,H+2K,\,*,\,0} + \frac{1}{3}L)$
4	—	Tetragonal	$\mid \hat{F}_{hkl} \mid^2 \leqslant \frac{1}{4} + \frac{1}{4}\hat{F}_{2h,\,2k,\,0} + \frac{1}{2}\hat{F}_{h-k,\,h+k,\,0}$
$\bar{4}$	—	Tetragonal	$\mid \hat{F}_{hkl} \mid^2 \leqslant \frac{1}{4} + \frac{1}{4}\hat{F}_{2h,\,2k,\,0} + \frac{1}{2} \mid \hat{F}_{h-k,\,h+k,\,2l} \mid \cos 2\pi\alpha_{h-k,\,h+k,\,2l}$
4_1	—	Tetragonal	$\mid \hat{F}_{hkl} \mid^2 \leqslant \frac{1}{4} + \frac{1}{4}(-1)^l \hat{F}_{2h,\,2k,\,0} + \frac{1}{2}(\cos 2\pi\frac{1}{4}l)\, \hat{F}_{h-k,\,h+k,\,0}$
4_2	—	Tetragonal	$\mid \hat{F}_{hkl} \mid^2 \leqslant \frac{1}{4} + \frac{1}{4}\hat{F}_{2h,\,2k,\,0} + \frac{1}{2}(-1)^l \hat{F}_{h-k,\,h+k,\,0}$
6	—	Hexagonal	$\mid \hat{F}_{HK*L} \mid^2 \leqslant \frac{1}{6} + \frac{1}{6}\hat{F}_{2H,\,2K,\,*,\,0} + \frac{1}{3}\hat{F}_{H-K,\,H+2K,\,*,\,0} + \frac{1}{3}F_{H,\,K,\,*,\,0}$
$\bar{6}$	$3/m$	Hexagonal	$\mid \hat{F}_{HK*L} \mid^2 \leqslant \frac{1}{6} + \frac{1}{6}\hat{F}_{0,\,0,\,*,\,2L} + \frac{1}{3} \mid \hat{F}_{H-K,\,H+2K,\,*,\,0} \mid \cos 2\pi\alpha_{H-K,\,H+2K,\,*,\,0} + \frac{1}{3} \mid \hat{F}_{H-K,\,H+2K,\,*,\,2L} \mid \cos 2\pi\alpha_{H-K,\,H+2K,\,*,\,2L}$
6_1	—	Hexagonal	$\mid \hat{F}_{HK*L} \mid^2 \leqslant \frac{1}{6} + \frac{1}{6}(-1)^L \hat{F}_{2H,\,2K,\,*,\,0} + \frac{1}{3}(\cos 2\pi\,\frac{1}{6}L)\, \hat{F}_{H-K,\,H+2K,\,*,\,0} + \frac{1}{3}(\cos 2\pi\,\frac{1}{6}L)\, \hat{F}_{H,\,K,\,*,\,0}$
6_2	—	Hexagonal	$\mid \hat{F}_{HK*L} \mid^2 \leqslant \frac{1}{6} + \frac{1}{6}\hat{F}_{2H,\,2K,\,*,\,0} + \frac{1}{3}(\cos 2\pi\,\frac{1}{3}L)\, \hat{F}_{H-K,\,H+2K,\,*,\,0} + \frac{1}{3}(\cos 2\pi\,\frac{1}{3}L)\, F_{H,\,K,\,*,\,0}$
6_3	—	Hexagonal	$\mid \hat{F}_{HK*L} \mid^2 \leqslant \frac{1}{6} + \frac{1}{6}(-1)^L \hat{F}_{2H,\,2K,\,*,\,0} + \frac{1}{3}\hat{F}_{H-K,\,H+2K,\,*,\,0} + \frac{1}{3}(-1)^L \hat{F}_{H,\,K,\,*,\,0}$
—	a	Monoclinic	$\mid \hat{F}_{hkl} \mid^2 \leqslant \frac{1}{2} + \frac{1}{2}(-1)^h \hat{F}_{0,\,2k,\,0}$

If the crystal possesses symmetry elements, more restrictive relations can be derived, just as in the more general case. For instance, suppose the crystal to have a mirror plane, m, in the x, z plane. Then there is an atom at x, $-y$, z for every atom at x, y, z. This gives formula (14) the form

$$^A\hat{F}_{hkl}=2\sum_{j=1}^{\frac{1}{2}N} n_j e^{-2\pi i(hx_j+lz_j)}\cos 2\pi ky_j.$$

On applying Cauchy's Inequality, one obtains

$$|\,^A\hat{F}_{hkl}\,|^2\leqslant 4\left(\sum_{j=1}^{\frac{1}{2}N} n_j\right)\frac{1}{2}\left(\sum_{j=1}^{\frac{1}{2}N} n_j(1+\cos 2\pi ky_j)\right)$$

or $$|\,^A\hat{F}_{hkl}\,|^2\leqslant \tfrac{1}{2}+\tfrac{1}{2}\,^A\hat{F}_{0,2k,0}, \qquad (17)$$

in exact analogy with the fourth entry in Table 1.

Further investigation shows that every relation in the table, as well as every other one derived similarly from the symmetry elements of a crystal, has the same form for $^A\hat{F}_{hkl}$ as for $\hat{F}_{hkl}$. It is therefore unnecessary to retain the superscript A. It is only necessary to note that the values of $\hat{F}_{hkl}$ can be made larger by dividing each one by the appropriate value of $\hat{f}$, and that the new, larger values provide much stronger inequalities—indeed, strong enough to be useful in practice.

The use of $\hat{f}$ in calculating $\hat{F}_{hkl}$ from F_{hkl}, as in formula (12), may be interpreted thus: The actual crystal contains atoms whose electron clouds are rather spread out; division of the amplitudes $\hat{F}_{hkl}=F_{hkl}/Z$ by $\hat{f}$ corresponds to correcting the observed F's to those of a crystal in which all the electrons of each atom are concentrated at its center. This correction can be made exactly only if the atoms in a crystal are all spherical and have the same f_j/Z_j. This is never really true, but in practical cases it turns out to be a very good approximation. The use of $\hat{f}$ is so valuable in strengthening the inequalities described here as to be almost essential.

In cases of crystals with large unit cells which contain many atoms it may be possible to divide the $\hat{F}_{hkl}$'s by numbers which decrease much more rapidly with increasing $(\sin\theta)/\lambda$ than do the values of $\hat{f}$. These numbers should correspond to 'unitary' structure factors of such atomic aggregates as can reasonably be assumed to be present in the crystal and to have approximate spherical symmetry. This procedure probably can be used only if the resolution of the Fourier series representing the crystal is insufficient to separate these aggregates into their constituent atoms. Such lack of resolution is quite usual in crystals with very large unit cells—the proteins provide several examples. The inequalities for these crystals can probably be considerably strengthened by such a procedure without seriously endangering their accuracy.

Relations limiting the phases of odd orders

All the inequalities derived so far limit the phases of only certain special Fourier coefficients. The inequality for the center of inversion, for example, so far provides limits on the signs of only the $F_{2h,2k,2l}$'s—those with all indices even. One can, however, obtain information on the phases of other coefficients.

First, consider a crystal with no symmetry. In this case

$$\hat{F}_{hkl}=\sum_{j=1}^{N} n_j e^{-2\pi i(hx_j+ky_j+lz_j)}.$$

Two different $\hat{F}_{hkl}$'s may be added, or subtracted, to give

$$\hat{F}_{hkl}\pm\hat{F}_{h'k'l'}=\sum_{j=1}^{N} n_j e^{-2\pi i(h'x_j+k'y_j+l'z_j)}\{e^{-2\pi i[(h-h')x_j+(k-k')y_j+(l-l')z_j]}\pm 1\}. \qquad (18)$$

Cauchy's Inequality applied to this expression leads to

$$|\,\hat{F}_{hkl}\pm\hat{F}_{h'k'l'}\,|^2\leqslant 2\pm 2\,|\,\hat{F}_{h-h',k-k',l-l'}\,|\cos 2\pi\,\alpha_{h-h',k-k',l-l'}. \qquad (19)$$

Further rearrangement brings one to the expression

$$|\,|\hat{F}_{hkl}|\,.\,|\hat{F}_{h'k'l'}|\cos 2\pi(\alpha_{hkl}-\alpha_{h'k'l'})-|\,\hat{F}_{h-h',k-k',l-l'}\,|\cos 2\pi(\alpha_{h-h',k-k',l-l'})\,|\leqslant 1-\tfrac{1}{2}(|\,\hat{F}_{hkl}\,|^2+|\,\hat{F}_{h'k'l'}\,|^2). \qquad (20)$$

This can be used to limit the ranges of α_{hkl} and $\alpha_{h-h',k-k',l-l'}$ if the value of $\alpha_{h'k'l'}$ is assumed. This is allowed, since the choice of origin is arbitrary in an asymmetric crystal.

An interesting special case of (20) arises by putting $h'=-h$, $k'=-k$, $l'=-l$. Since $\alpha_{\bar{h}\bar{k}\bar{l}}=-\alpha_{hkl}$ and $|\,\hat{F}_{\bar{h}\bar{k}\bar{l}}\,|=|\,\hat{F}_{hkl}\,|$, one obtains

$$|\,|\hat{F}_{hkl}\,|^2\cos 2\pi(2\alpha_{hkl})-|\,\hat{F}_{2h,2k,2l}\,|\cos 2\pi\alpha_{2h,2k,2l}\,|\leqslant 1-|\,\hat{F}_{hkl}\,|^2. \qquad (20')$$

It is always possible to choose the origin so as to make α_{hkl} vanish. Choosing the origin in this way, we have, by simple rearrangements,

$$|\,\hat{F}_{hkl}\,|^2\leqslant\tfrac{1}{2}(1+|\,\hat{F}_{2h,2k,2l}\,|\cos 2\pi\alpha_{2h,2k,2l}). \qquad (20'')$$

This inequality shows that, for any crystal,

$$|\,\hat{F}_{hkl}\,|^2\leqslant\tfrac{1}{2}\quad\text{if}\quad|\,\hat{F}_{2h,2k,2l}\,|=0.$$

More useful expressions are obtained in case the crystal possesses symmetry. For instance, the simple case of a center of inversion leads to

$$|\,2\hat{F}_{hkl}\hat{F}_{h'k'l'}-(\hat{F}_{h+h',k+k',l+l'}+\hat{F}_{h-h',k-k',l-l'})\,|\leqslant 1+\tfrac{1}{2}(\hat{F}_{2h,2k,2l}+\hat{F}_{2h',2k',2l'})-(\hat{F}^2_{hkl}+\hat{F}^2_{h'k'l'}), \qquad (21)$$

or

$$|\,2\hat{F}_{hkl}\hat{F}_{h'k'l'}-(\hat{F}_{h+h',k+k',l+l'}+\hat{F}_{h-h',k-k',l-l'})\,|\leqslant 1+\hat{F}_{h+h',k+k',l+l'}\hat{F}_{h-h',k-k',l-l'}-(\hat{F}^2_{hkl}+\hat{F}^2_{h'k'l'}), \qquad (22)$$

depending on the choice of a_j in Cauchy's Inequality, (15). Formulas (21) and (22) can be used to find the signs of $\hat{F}$'s that do not yield to the simpler inequalities of Table 1, many of which can prove an $\hat{F}$ to be positive, but not the reverse. In such cases, (21) and (22) can prove some of the $\hat{F}$'s to be negative.

Another very important use of (21) and (22) is in limiting the signs of $\hat{F}_{hkl}$'s with h, k, l not all even. This is done as follows: Suppose that the signs of the $\hat{F}_{2h,2k,2l}$'s have been found—from the inequalities in Table 1 or from (21) and (22)—then choose h, k, l and h', k', l' in (21) or (22) such that $h+h'$, $k+k'$, $l+l'$ are all even, but h, k, l, h', k', l' are not. Then, in principle, the signs of all the terms in (21) and (22), except those of $\hat{F}_{hkl}$ and $\hat{F}_{h'k'l'}$ are known. If the sign of one of these is assumed, that of the other follows. This knowledge then allows the signs of other $\hat{F}_{hkl}$'s to be found. This procedure could lead to determinations of the signs of all the $\hat{F}_{hkl}$'s, except for a certain ambiguity in the signs of those that have h, k and l not all even, since these signs depend on the assumption just mentioned. This ambiguity is due to the eight possible choices of origin in a crystal possessing a center of symmetry, for between each two identical centers is another center not identical with the first kind. The structure can be described in terms of a Fourier series about either kind of center and the two series will have the same $F_{2h,2k,2l}$'s, but will have opposite signs for some other F's. It is interesting that this ambiguity in choice of origin corresponds to an ambiguity in the signs of just the proper sets of F's.

The addition and subtraction of two F's yields extremely powerful inequalities when other symmetry elements than the center are used. Examples of some of these will be presented later in this paper.

Combinations of symmetry elements

New and important inequalities can be derived for crystals having more than one symmetry element. For instance, consider the simple case of a two-fold axis and a mirror plane normal to it, such as occurs in the space group C_{2h}^1-P2/m. The co-ordinates of the general atomic position can be taken as

$$x, y, z; \quad x, \bar{y}, z; \quad \bar{x}, y, \bar{z}; \quad \bar{x}, \bar{y}, \bar{z}.$$

Accordingly, the formula for $\hat{F}_{hkl}$ is

$$\hat{F}_{hkl}=4\sum_{j=1}^{\frac{1}{8}N} n_j \cos 2\pi k y_j \cos 2\pi (hx_j+lz_j). \qquad (23)$$

Cauchy's Inequality applied to this expression can yield two different results, depending on whether a_j in formula (15) is taken to be $n_j^{\frac{1}{2}}$ or $n_j^{\frac{1}{2}}\cos 2\pi k y_j$. These two choices of a_j yield, respectively,

$$\hat{F}_{hkl}^2 \leqslant \tfrac{1}{4}(1+\hat{F}_{0,2k,0}+\hat{F}_{2h,0,2l}+\hat{F}_{2h,2k,2l}) \qquad (24)$$

and

$$\hat{F}_{hkl}^2 \leqslant \tfrac{1}{4}(1+\hat{F}_{0,2k,0})(1+\hat{F}_{2h,0,2l}). \qquad (25)$$

Formula (25) can also be written

$$\hat{F}_{hkl}^2 \leqslant \tfrac{1}{4}(1+\hat{F}_{0,2k,0}+\hat{F}_{2h,0,2l}+\hat{F}_{0,2k,0}\hat{F}_{2h,0,2l}). \qquad (26)$$

Comparing (24) and (26), one sees that $\hat{F}_{2h,2k,2l}$ and the product $\hat{F}_{0,2k,0}\cdot\hat{F}_{2h,0,2l}$ play analogous roles in these two inequalities. These two numbers are not equal, in general, and one or the other of these inequalities is the more powerful, depending on circumstances. Quite commonly it happens that such formulas as (24) and (25) provide sign determinations when those derived from a single symmetry element do not. This can arise from one of the following situations: (*a*) the signs of some of the terms of the right sides of (24) and (25) are already known; or (*b*) one of $\hat{F}_{0,2k,0}$ or $\hat{F}_{2h,0,2l}$ is zero or small, the other then being subject to a very powerful inequality in (25), equivalent to dividing by two the right-hand side of the inequality for one symmetry element alone (cf. formulas (9) and (17)).

If Cauchy's Inequality is applied to the sums and differences of two $\hat{F}_{hkl}$'s belonging to a crystal of symmetry C_{2h}^1-P2/m, the following inequality may be obtained (for the case of $a_j=n_j^{\frac{1}{2}}$)

$$\begin{aligned}(\hat{F}_{hkl}\pm\hat{F}_{h'k'l'})^2 \leqslant \tfrac{1}{4}\{&2+\hat{F}_{0,2k,0}+\hat{F}_{2h,0,2l}+\hat{F}_{2h,2k,2l}\\ &+\hat{F}_{0,2k',0}+\hat{F}_{2h',0,2l'}+\hat{F}_{2h',2k',2l'}\\ &\pm 2[\hat{F}_{h-h',k-k',l-l'}+\hat{F}_{h-h',k+k',l-l'}\\ &+\hat{F}_{h+h',k-k',l+l'}+\hat{F}_{h+h',k+k',l+l'}]\}. \qquad (27)\end{aligned}$$

This relation can be used as a tool more powerful than (24) or (25) for finding the negative $\hat{F}$'s and the $\hat{F}$'s with hkl not all even. Its increased power arises from the use in its derivation of more symmetry elements than the center alone.

Each space-group symmetry can be made to yield a set of characteristic inequalities, and they become more powerful as the number of symmetry elements increases. In illustration of this increase in power, we present some of the inequalities which can be derived for the space group $D_{2h}^{12}-Pnnm$. This space group provides the general atomic positions:

$$x, y, z; \ \bar{x}, \bar{y}, z; \ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}-z; \ \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}-z;$$

$$\bar{x}, \bar{y}, \bar{z}; \ x, \ y, \ \bar{z}; \ \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}+z; \ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}+z.$$

Accordingly, the unitary structure factor for the space group is

$$\hat{F}_{hkl}=8\sum_{j=1}^{\frac{1}{8}N} n_j \cos 2\pi h x_j \cos 2\pi k y_j \cos 2\pi l z_j,$$

if $h+k+l$ is even,

or

$$\hat{F}_{hkl}=-8\sum_{j=1}^{\frac{1}{8}N} n_j \sin 2\pi k x_j \sin 2\pi k y_j \cos 2\pi l z_j,$$

if $h+k+l$ is odd.

Four different inequalities can then be derived from these formulas, depending on the choice of a in (15). These are listed below:

$$\hat{F}^2_{hkl} \leqslant \tfrac{1}{8}\{1+\hat{F}_{0,0,2l}+\hat{F}_{2h,2k,0}+\hat{F}_{2h,2k,2l}+(-1)^{h+k+l} \times (\hat{F}_{2h,0,0}+\hat{F}_{0,2k,0}+\hat{F}_{2h,0,2l}+\hat{F}_{0,2k,2l})\}, \quad (28)$$

$$\hat{F}^2_{hkl} \leqslant \tfrac{1}{8}\{1+\hat{F}_{0,0,2l}\}\{1+\hat{F}_{2h\ 2k,0}+(-1)^{h+k+l} \times (\hat{F}_{2h,0,0}+\hat{F}_{0,2k\ 0})\}, \quad (29)$$

$$\hat{F}^2_{hkl} \leqslant \tfrac{1}{8}\{1+(-1)^{h+k+l}\hat{F}_{0.2k,0}\}\{1+\hat{F}_{0,0,2l}+(-1)^{h+k+l} \times (\hat{F}_{2h,0,0}+\hat{F}_{2h,0,2l})\}, \quad (30)$$

$$\hat{F}^2_{hkl} \leqslant \tfrac{1}{8}\{1+(-1)^{h+k+l}\hat{F}_{2h,0,0}\}\{1+\hat{F}_{0,0,2l}+(-1)^{h+k+l} \times (\hat{F}_{0,2k,0}+\hat{F}_{0,2k,2l})\}. \quad (31)$$

In addition to these, there are a number of valuable 'sum and difference' relations for *Pnnm*; among them the following:

$$\begin{aligned}(\hat{F}_{hkl} \pm \hat{F}_{h'k'l'})^2 \leqslant \tfrac{1}{8}\{&2+\hat{F}_{0,0,2l}+\hat{F}_{0,0,2l'}+\hat{F}_{2h,2k,0}\\ &+\hat{F}_{2h',2k',0}+\hat{F}_{2h,2k,2l}+\hat{F}_{2h',2k',2l'}\\ &+(-1)^{h+k+l}(\hat{F}_{2h,0,0}+\hat{F}_{0,2k,0}+\hat{F}_{2h,0,2l}+\hat{F}_{0,2k,2l})\\ &+(-1)^{h'+k'+l'}(\hat{F}_{2h',0,0}+\hat{F}_{0,2k',0}+\hat{F}_{2h',0,2l'}+\hat{F}_{0,2k',2l'})\\ &\pm 2\,[\hat{F}_{h+h',k+k',l+l'}+\hat{F}_{h+h',k+k',l-l'}+\hat{F}_{h-h',k-k',l+l'}\\ &+\hat{F}_{h-h',k-k',l-l'}+(-1)^{h'+k'+l'}(\hat{F}_{h+h',k-k',l+l'}\\ &+\hat{F}_{h+h',k-k',l-l'}+\hat{F}_{h-h',k+k',l+l'}+\hat{F}_{h-h',k+k',l-l'})]\}, \end{aligned} \quad (32)$$

$$\begin{aligned}(\hat{F}_{hkl} \pm \hat{F}_{h'k'l})^2 \leqslant \tfrac{1}{8}\{&2+2\hat{F}_{0,0,2l}+\hat{F}_{2h',2k',0}+\hat{F}_{2h,2k,0}\\ &+\hat{F}_{2h,2k,2l}+\hat{F}_{2h',2k',2l}\\ &+(-1)^{h+k+l}(\hat{F}_{2h,0,0}+\hat{F}_{0,2k,0}+\hat{F}_{2h,0,2l}+\hat{F}_{0,2k,2l})\\ &+(-1)^{h'+k'+l}(\hat{F}_{2h',0,0}+\hat{F}_{0,2k',0}+\hat{F}_{2h',0,2l}+\hat{F}_{0,2k',2l})\\ &\pm 2\,[\hat{F}_{h-h',k-k',0}+\hat{F}_{h+h',k+k',0}+\hat{F}_{h+h',k+k',2l}\\ &+\hat{F}_{h-h',k-k',2l}\\ &+(-1)^{h'+k'+l}(\hat{F}_{h-h',k+k',0}+\hat{F}_{h+h',k-k',0}\\ &+\hat{F}_{h-h',k+k',2l}+\hat{F}_{h+h',k-k',2l})]\}, \end{aligned} \quad (33)$$

$$\begin{aligned}(\hat{F}_{hkl} \pm \hat{F}_{h'k'l})^2 \leqslant \tfrac{1}{8}\{&1+\hat{F}_{0,0,2l}\}\{2+\hat{F}_{2h,2k,0}+\hat{F}_{2h',2k',0}\\ &+(-1)^{h+k+l}(\hat{F}_{2h,0,0}+\hat{F}_{0,2k,0})+(-1)^{h'+k'+l}\\ &\times(\hat{F}_{2h',0,0}+\hat{F}_{0,2k',0})\\ &\pm 2\,[\hat{F}_{h+h',k+k',0}+\hat{F}_{h-h',k-k',0}+(-1)^{h'+k'+l}\\ &\times(\hat{F}_{h-h',k+k',0}+\hat{F}_{h+h',k-k',0})]\}. \end{aligned} \quad (34)$$

From these can be derived others by giving special values to the indices. For instance, by putting $l=0$ in (33) or (34), one obtains:

$$\begin{aligned}(\hat{F}_{hk0} \pm \hat{F}_{h'k'0})^2 \leqslant \tfrac{1}{4}\{&2+\hat{F}_{2h,2k,0}+\hat{F}_{2h',2k',0}+(-1)^{h+k}\\ &\times(\hat{F}_{2h,0,0}+\hat{F}_{0,2k,0})+(-1)^{h'+k'}(\hat{F}_{2h',0,0}+\hat{F}_{0,2k'\ 0})\\ &\pm 2\,[\hat{F}_{h-h',k-k',0}+\hat{F}_{h+h',k+k',0}+(-1)^{h'+k'}\\ &\times(\hat{F}_{h-h',k+k',0}+\hat{F}_{h+h',k-k',0})]\}. \end{aligned} \quad (35)$$

Also, by letting $h=h'$, $k=k'$, $l=l'$ in (32) and (34), one obtains, respectively, (28) and (29).

The space group *Pnnm* can lead to an immense number of inequalities—the authors have derived about thirty—which differ in the special values of h, k, l and h', k', l' used in their derivation, and in the way in which a_j is chosen in (15). In addition to these, the inequalities derived from any subgroup of *Pnnm* are also applicable to crystals with this space group. Thus it seems out of place to attempt an exhaustive list of inequalities for even this one space group in the present paper. For any particular space group, a set of inequalities can be derived as needed. Different members of this set are useful in sign (or phase) determinations for different $\hat{F}_{hkl}$'s. The process is laborious, but not difficult; its essentials have been outlined in the early parts of this paper.

Application of the inequalities

Gillis (1948) has presented a beautiful example of the usefulness of formulas (8) and (22) in finding the signs of the $\hat{F}_{h0l}$'s for oxalic acid dihydrate, using the data of Robertson & Woodward (1936). This work illustrates in detail the process of finding the signs of F's in an actual case. The authors of this paper are applying the inequalities in the course of an investigation into the structure of crystalline dekaborane, $B_{10}H_{14}$. It is hoped to publish the results of this work in the near future, at which time the details of the sign determinations involved will be presented.

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