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The Determination of Signs of Structure Factors from the Intensities

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It is shown that in principle the magnitudes and signs of certain structure factors can be calculated from a sufficient range of X-ray intensities. The range provided by experiment will seldom be enough to make the results of practical value.

Introduction

A routine procedure which does not require previous knowledge of any signs has been developed by Hauptman & Karle (1953) for determining the signs of the structure factors for space group $P\bar{1}$. Their claim that the procedure is valid for crystals of any complexity, given only a knowledge of a sufficient number of X-ray intensities, is, however, incorrect, as has been pointed out by Vand & Pepinsky (1953, 1954) and by Cochran & Woolfson (1954). In the following sections a method is described by which both the magnitudes and the signs of certain structure factors (one-eighth of the total for space group $P\bar{1}$) can in principle be calculated from a sufficient range of intensities. The results hold for centrosymmetric crystals and for some non-centrosymmetric crystals, but unfortunately the auxiliary conditions are so restrictive as to make the results of no value for the practical determination of any but the simplest crystal structures.

Derivation for space group $P\bar{1}$

The physical basis of the result is roughly as follows. Suppose that N equal atoms per unit cell have coordinates $\pm\mathbf{r}_i$, $i = 1, 2, \dots, \frac{1}{2}N$. The corresponding Patterson function has N peaks of weight 1 at points $\pm 2\mathbf{r}_i$ and $\frac{1}{2}(N^2 - 2N)$ peaks of weight 2 at $\pm(\mathbf{r}_i \pm \mathbf{r}_j)$, $i \neq j$. In the squared Patterson function the weights of peaks belonging to these two classes are therefore 1 and 4 respectively. By multiplying the Patterson function by 2, and subtracting from it a modification of the squared Patterson function, all peaks except those at $\pm 2\mathbf{r}_i$ can be cancelled out, and the positions of these remaining peaks bear an obvious relation to

the atomic positions. These functions and operations have each a counterpart in reciprocal space, and when expressed in terms of structure factors the result is a relation between those structure factors whose indices are all even, and the intensities.

To simplify the derivation, we take the atoms to have scattering factors $f = 1$ for all values of $s = 2 \sin \theta / \lambda$, that is, they are point atoms. The peaks of the Patterson function then have scattering factors (more correctly, Fourier transforms) $f^2 = 1$, from which it follows that the density distribution in an atomic peak and in a Patterson peak is the same. We now define

$$F(\mathbf{h}) = 2 \sum_{j=1}^{\frac{1}{2}N} \cos 2\pi\mathbf{h} \cdot \mathbf{r}_j, \quad (1)$$

$$\varrho(\mathbf{r}) = \sum_{s < s_0} \mathbf{h} F(\mathbf{h}) \cos 2\pi\mathbf{h} \cdot \mathbf{r}, \quad (2)$$

$$P(\mathbf{r}) = \sum_{s < s_0} \mathbf{h} F^2(\mathbf{h}) \cos 2\pi\mathbf{h} \cdot \mathbf{r}. \quad (3)$$

From (1) it may be shown that

$$F^2(\mathbf{h}) = N + F(2\mathbf{h}) + 2 \sum_{\substack{m=+\frac{1}{2}(N^2-2N) \\ m=-\frac{1}{2}(N^2-2N)}} \cos 2\pi\mathbf{h} \cdot \mathbf{r}_m, \quad (4)$$

where $\mathbf{r}_m = \mathbf{r}_i - \mathbf{r}_j$, $i \neq j$.

The summation over \mathbf{h} is over all reciprocal-lattice points which lie inside a sphere of radius s_0 . (The value of s_0 will be considered later.)

We now define

$$\varrho^2(\mathbf{r}) = \sum_{s < 2s_0} \mathbf{h} G(\mathbf{h}) \cos 2\pi\mathbf{h} \cdot \mathbf{r}. \quad (5)$$

It then follows (Sayre, 1952) that

$$G(\mathbf{h}) = \sum_{\mathbf{h}'} F(\mathbf{h}')F(\mathbf{h}+\mathbf{h}'), \quad (6)$$

and that

$$G(\mathbf{h}) = g(h)F(\mathbf{h}), \quad (7)$$

where $g(h)$ is the Fourier transform of a peak in the function $\rho^2(\mathbf{r})$. In this case it is also the transform (scattering factor) of a peak of unit weight in the function $P^2(\mathbf{r})$. In (6), the summation over \mathbf{h}' is over all reciprocal-lattice points which are common to two limiting spheres whose centres are on points 0 and \mathbf{h} respectively, and which both have radius s_0 . Suppose there are $n(h)$ such points.

From (6) and (7)

$$g(h)F(\mathbf{h}) = n(h) \overline{F(\mathbf{h}')F(\mathbf{h}+\mathbf{h}')}. \quad (8)$$

If we now introduce unitary structure factors $U(\mathbf{h}) = F(\mathbf{h})/N$, and make use of the result

$$U(\mathbf{h}) = N \overline{U(\mathbf{h}')U(\mathbf{h}+\mathbf{h}')},$$

(Cochran, 1953; Hughes, 1953), then (8) reduces to

$$g(h) = n(h). \quad (9)$$

Next we define

$$P^2(\mathbf{r}) = \sum_{s < 2s_0} Q(\mathbf{h}) \cos 2\pi\mathbf{h} \cdot \mathbf{r}, \quad (10)$$

so that

$$\begin{aligned} Q(\mathbf{h}) &= \sum_{\mathbf{h}'} F^2(\mathbf{h}')F^2(\mathbf{h}+\mathbf{h}') \\ &= n(h) \overline{F^2(\mathbf{h}')F^2(\mathbf{h}+\mathbf{h}')}. \end{aligned} \quad (11)$$

But $Q(\mathbf{h})$, being a Fourier coefficient of the squared Patterson function $P^2(\mathbf{r})$, can be written

$$Q(\mathbf{h}) = g(h) \left(N^2 + F(2\mathbf{h}) + 4 \sum_{m=-\frac{1}{2}(N^2-2N)}^{m=\frac{1}{2}(N^2-2N)} \cos 2\pi\mathbf{h} \cdot \mathbf{r}_m \right), \quad (12)$$

since $P^2(\mathbf{r})$ has a peak of weight N^2 at $\mathbf{r} = 0$, N peaks of weight 1 at $\pm 2\mathbf{r}_j$ and $\frac{1}{2}(N^2-2N)$ peaks of weight 4 at $\mathbf{r}_m = \mathbf{r}_i \pm \mathbf{r}_j$. Furthermore, it has already been pointed out that each peak of unit weight in $P^2(\mathbf{r})$ has a 'scattering factor' $g(h)$. Combining (4), (9), (11) and (12), by elimination we obtain

$$F(2\mathbf{h}) = 2\{F^2(\mathbf{h}) - N\} - \{\overline{F^2(\mathbf{h}')F^2(\mathbf{h}+\mathbf{h}')} - N^2\}. \quad (13a)$$

This result relates a structure factor to the intensities.

If the F 's do not correspond to point atoms, (13a) should be written as

$$U(2\mathbf{h}) = 2\{NU^2(\mathbf{h}) - 1\} - N\{\overline{N^2U^2(\mathbf{h}')U^2(\mathbf{h}+\mathbf{h}')} - 1\}. \quad (13b)$$

If we now define $E(\mathbf{h}) = N^{\frac{1}{2}}U(\mathbf{h})$, and make use of the fact that $\overline{E^2(\mathbf{h})} = 1$, (13a) may be written

$$E(2\mathbf{h}) = N^{\frac{1}{2}}[2\{E^2(\mathbf{h}) - 1\} - N\{\overline{E^2(\mathbf{h}') - 1}\}\{E^2(\mathbf{h}+\mathbf{h}') - 1\}]. \quad (13c)$$

If only the sign of a structure factor is required,

$$S(2\mathbf{h}) = S[2\{E^2(\mathbf{h}) - 1\} - N\{\overline{E^2(\mathbf{h}') - 1}\}\{E^2(\mathbf{h}+\mathbf{h}') - 1\}]. \quad (14)$$

We may compare this with Hauptman & Karle's result, which, for the case we are considering where only intensities are available for sign determination, is

$$\begin{aligned} S(2\mathbf{h}) &= S[2\{E^2(\mathbf{h}) - 1\} \\ &\quad + \frac{1}{N} \sum_{\mathbf{h}'} \{E^2(\mathbf{h}') - 1\}\{E^2(\mathbf{h}+\mathbf{h}') - 1\}]. \end{aligned} \quad (15)$$

The two results do not agree. This is to be expected, since (15) corresponds to equating $\rho(\mathbf{r})$, with linear dimensions increased twofold, to a weighted sum of $P(\mathbf{r})$ and $P^2(\mathbf{r})$, as has already been pointed out elsewhere.

Is (13b) likely to be of practical value? First, it applies only when the atoms are equal. Secondly, the average of $U^2(\mathbf{h}')U^2(\mathbf{h}+\mathbf{h}')$ must be taken over a sufficiently great range of indices. The physical basis of (13b) shows that by 'sufficiently great', we mean that the radius of the limiting sphere s_0 must be such that if a Patterson function were calculated with values of $U^2(\mathbf{h})$ as coefficients, it would be found to contain completely resolved spherically symmetric peaks. Equation (14) may be expected to hold even when this condition is relaxed, at least when $|U(2\mathbf{h})|$ is comparatively large; but with the range of data provided by experiment, even (14) may be expected to break down frequently if N is greater than about 6.

The result (14) may find some application to crystals which contain a considerable number of atoms per unit cell, of which some four or six are equal and of considerably greater atomic number than the remainder. When the structure contains only two heavy atoms per unit cell it is in principle correct to equate $S(2\mathbf{h})$ to the sign of either term on the right-hand side of (15), but in this instance it would be more realistic to evaluate the Patterson function, and then calculate the signs of *all* the structure factors (and not merely those with all indices even) from the coordinates of the heavy atom.

Derivation for other space groups

Somewhat different relations can be found which apply to other centrosymmetric space groups. For example, for space group $P2_1/a$ there is a definite relation between the section through the Patterson function at $y = \frac{1}{2}$, and the projection of the electron density on a parallel plane. An analysis similar to that given above shows that it then follows that

$$U(2h, 0, 2l) = N\{(-1)^{h+k} \overline{U^2(hkl)}\}, \quad (16)$$

so that

$$S(2h, 0, 2l) = S[(-1)^{h+k} \{\overline{E^2(hkl)} - 1\}]. \quad (17)$$

The average is over a range of values of k . The conditions that must be satisfied for (16) to hold rigorously are the same as were described in the previous section. The result (17) may be expected to hold even when they are relaxed, especially if $|U(2h, 0, 2l)|$ is fairly large. The result (17) is in this case identical with

that obtained by the statistical method of Hauptman & Karle (1953, p. 50). The connection between (17) and a Patterson-Harker section has already been pointed out by Vand & Pepinsky (1953); it is mentioned here for the sake of completeness. Once again, the result will be of practical value only for simple crystal structures, or when the asymmetric unit includes some small number of approximately equal heavy atoms.

Similar results can be found for space groups which do not have a centre of symmetry, provided that they project to give a centrosymmetric plane group. For example, for space group $P2$

$$U(2h,0,2l) = \overline{\{NU^2(hkl)-1\}}, \quad (18)$$

while for space group $P2_1$

$$U(2h,0,2l) = N\overline{\{(-1)^k U^2(hkl)\}}. \quad (19)$$

The same remarks apply to these two results as have been made about earlier ones.

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A New Photographic Method for Studying the Texture of Large Single Crystals

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The orientation, in one plane, of macromosaic regions covering a crystal face several centimetres long may be determined from one photograph of the reflection pattern of characteristic radiation when the film-to-crystal distance is made large compared with that between crystal and X-ray source, and a grid placed in front of the film is rotated in synchronism with the crystal rotation. A line X-ray source parallel with the crystal rotation axis is used. The reflections are rapidly interpreted with the aid of a master pattern given by a good crystal which need not be of same material as the specimen.

Introduction

In order to assist the selection of suitable crystal specimens for use as monochromators it is desirable to develop methods for the X-ray examination of the reflecting planes which will give as much information as possible about the variation, over the surface of the plane, of the reflecting power, sharpness of reflection, and any large-scale misorientations that may be present. Good quality monochromators are required not only in diffraction work but also in the rapidly widening field of fluorescence analysis. Knowledge of the above properties also plays a part in studies of crystal growth and deformation.

A number of methods exist which will give some of the required data, though possibly only in qualitative

form. It is interesting to note that for space groups $P6_1$, $P6_12$ and $R3$ the magnitudes and signs of all structure factors in one zone can in principle be calculated from the general intensities. This is an immediate deduction from the work of Buerger (1946).

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