Acta Cryst. (1955). 8, 27

The Production of Fibre Diagrams with the Optical Diffraction Spectrometer

By A. R. Stokes

Wheatstone Physics Laboratory, King's College, London W. C. 2, England

(*Received* 13 *July* 1954)

Two methods are described for producing a fibre diagram of a given structure by superimposing the diffraction patterns of a number of projections of the structure. An expression is obtained for the minimum number of projections required for a faithful representation of the fibre diagram.

An X-ray fibre diagram, like a rotation photograph of a single crystal, is the result of superimposing diffraction patterns of the fibre unit in all orientations which have the fibre axis in a given direction. If we wish to use the diffraction spectrometer (Hughes & Taylor, 1953) for producing a fibre diagram of a trial structure, we must obtain projections of the structure on all planes parallel to the fibre axis and superimpose the diffraction patterns of these projections. In practice, of course, we can use only a finite number of projections; the minimum permissible number is discussed below. The first question that arises is how to superimpose the diffraction patterns that are obtained optically. Two simple methods are proposed here:

(1) A number of projections of the structure are prepared, and are punched on separate masks. Each mask is inserted in the diffraction spectrometer for the same length of time, and a photographic film is exposed to the diffraction patterns so that the intensities of diffraction of all the patterns are added together on the film. Each mask must be inserted in the diffraction spectrometer with its fibre axis parallel to a fixed direction in the apparatus, otherwise the result will be a disoriented fibre diagram. This method has the disadvantage that the fibre diagram cannot be viewed directly.

(2) A number of projections of the structure are plotted out, and all are punched on the same mask with their fibre axes parallel. They must be distributed fairly widely over the useful area of the mask, with blank areas between them of at least the same order of width as the diameter of the structure itself. The resulting diffraction pattern will be crossed by fine fringes due to interference between one projection, taken as a whole, and another; but if the resolving power of the instrument is made insufficient to detect these fringes (by making the source pin-hole just large enough to blur out the fringes) then the resulting pattern will be the result of adding the intensities (*not* the amplitudes) of the separate patterns. It is essential that the intensity of illumination be uniform all over the mask, otherwise some projections will contribute more to the final pattern than others.

This method can be used for viewing the fibre pattern directly, but it suffers from the disadvantage that each projection can occupy only a small fraction of the area of the mask, and so, with a given minimum size of punch, the number of atoms that can be represented without overlapping is much smaller than in method (1).

We must now consider how many projections are needed to give a fibre diagram sensibly the same as that given by an infinite number. This depends on the size of the region of reciprocal space to be covered. An empirical approach to the problem is to take a number of projections at equally-spaced angular intervals and photograph their superimposed diffraction pattern; then to take the same number of projections in directions mid-way between the first set of directions and photograph their diffraction pattern. For instance, the first set of projections might be made at angles of 0, 45, 90, 135° to a fixed direction (the pattern repeats itself after 180°), and the second at $22\frac{1}{2}$, $67\frac{1}{2}$, $112\frac{1}{2}$ and $157\frac{1}{2}$°. It will be found that the two patterns will be identical within a certain distance from the meridional axis, and will differ outside this region. This is illustrated in Fig. 2(*a*) and (*b*), which shows the diffraction patterns of two projections of a helix with eight 'atoms' per turn, as in Fig. 1(*a*) and (*b*). Since rotation of this helix through 45° does not change the projection, a single projection will give the same result as four at 0, 45, 90 and 135°. We can

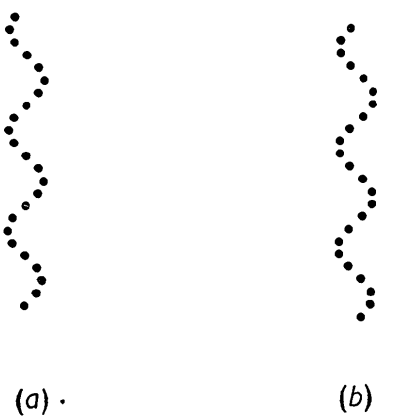

Fig. 1. Two projections of a helical structure.

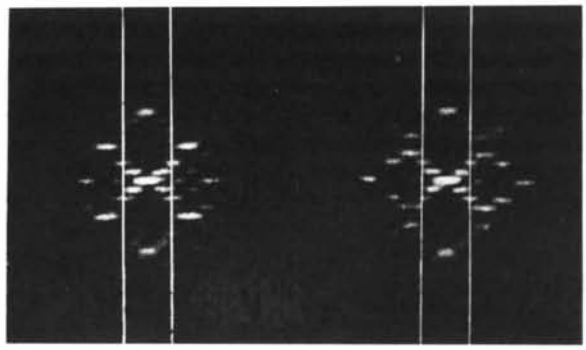

Fig. 2. (*a*) and (*b*). Diffraction patterns of the projections shown in Fig. 1(*a*) and (*b*) respectively.

see that the diffraction patterns are similar in the region between the parallel lines, but differ outside this region. We may assume that each diffraction pattern represents the fibre diagram reliably inside the region indicated, but not outside this region. If we superimpose the patterns in Fig. 2(*a*) and Fig. 2(*b*). we should expect the resulting pattern to be reliable over a wider region, and the analysis given later will confirm this.

Fig. 3(*a*) shows the result of superimposing the two diffraction patterns photographically, while Fig. 3(*b*) shows the result of using the second method described above; here the fringes crossing the pattern can be seen clearly.

The question of the number of projections can be approached analytically as follows. Let $P(r, \varphi, z)$ be the Patterson function of the structure at a point whose cylindrical coordinates are (r, φ, z). The intensity at a point in reciprocal space with cylindrical coordinates (ξ, ψ, ζ) is then proportional to

$$I = \int P(r, \varphi, z).\exp\,[2\pi i(r\xi\cos\varphi\cos\psi + r\xi\sin\varphi\sin\psi + z\zeta)]r.dr.d\varphi.dz$$
$$= \int P(r, \varphi, z).\exp\,[2\pi i\{r\xi\cos(\psi-\varphi)+z\zeta\}] \times r.dr.d\varphi.dz\,. \quad (1)$$

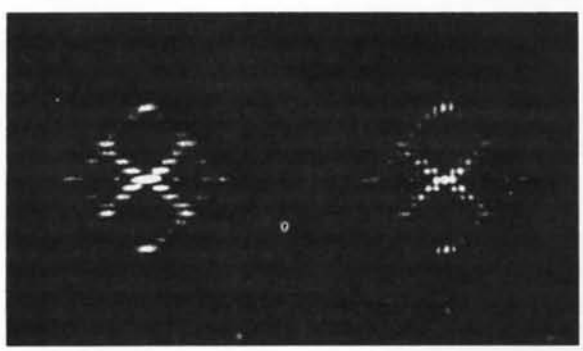

Fig. 3. (*a*) Superimposed diffraction patterns of projections shown in Fig. 1(*a*) and (*b*).
(*b*) Diffraction pattern of the projections in Fig. 1 placed side by side.

The fibre diagram represents the average of this function over all ψ from 0° to 360°, and we want to find under what conditions the average over a given number of discrete values of ψ will be nearly equal to the continuous average. We can do this if we represent the expression (1) by its Fourier series with respect to ψ; this is

$$I(\xi, \psi, \zeta) = A_0+A_1\exp(i\psi)+A_2\exp(2i\psi)+\ldots + A_{-1}\exp(-i\psi)+A_{-2}\exp(-2i\psi)+\ldots\,, \quad (2)$$

where

$$A_n = \int P(r, \varphi, z).\exp.in(\tfrac{1}{2}\pi-\varphi).J_n(2\pi r\xi) \times \exp(2\pi i\zeta z).r.dr.d\varphi.dz\,, \quad (3)$$

in which $J_n(x)$ is the nth-order Bessel function of the first kind, which, by one of its definitions, is equal to the nth Fourier component of $\exp(ix\sin\psi)$.

If we take the average of $I(\xi, \psi, \zeta)$ as expressed in (2), over n equally spaced values of ψ, we obtain

$$\bar{I}(\xi, \zeta) = A_0+A_n\exp(in\psi')+A_{2n}\exp(2in\psi')+\ldots + A_{-n}\exp(-in\psi')+A_{-2n}\exp(-2in\psi')+\ldots\,, \quad (4)$$

where ψ' is the angle made by one of the projections (it is immaterial which) with the standard direction. This will be independent of ψ' and equal to A_0, the true average, if A_n and all higher-order Fourier coefficients are negligibly small.

Now Bessel functions have the property that $J_n(x)$ is negligibly small (as may be verified from tables) for all values of x less than about $n-3$, for the range of values of n in which we are interested. It follows from equation (3) that A_n is negligibly small for all values of ξ such that

$$2\pi r\xi < n-3 \quad (5)$$

for the largest value of r encountered in the Patterson diagram of the fibre structure, that is, if

$$2\pi D\xi < n-3\,, \quad (6)$$

where D is the diameter of the structural unit.

If $\xi_{\max.}$ is the largest value of ξ for which the pattern is correct, its reciprocal will be $d_{\min.}$, the smallest spacing that can be correctly represented. The smallest value of n that we can use is

$$n = 2\pi D/d_{\min.}+3\,. \quad (7)$$

It may be more convenient to express this in terms of the maximum angle $\alpha = 2\pi/n$ between the projections; the relation then becomes

$$\frac{1}{\alpha} = \frac{D}{d_{\min.}}+\frac{3}{2\pi}\,. \quad (8)$$

In the example illustrated in Figs. 1 and 2, $n = 8$, and we should therefore expect

$$2\pi D/d_{\min.} = 5\,.$$

In Fig. 2 the parallel lines have been drawn at

$$2\pi D/d_{\min.} = 6$$

(that is, at $2\pi r_0\xi = 3$, where r_0 is the radius of the helix) and equation (7) is therefore a little too stringent when applied to this case.

An interesting feature of Fig. 3(*b*) is that distinct fringes appear in the regions in which Fig. 2(*a*) and Fig. 2(*b*) are identical, but not in all other regions. In particular, there are no fringes on the fourth layer line, since one of the diffraction patterns contributes nothing to this layer line. Thus the pattern in Fig. 3(*b*) tells us something about the variation of diffracted amplitude with ψ as well as giving the mean intensity as ψ is varied.

Reference

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Acta Cryst. (1955). **8**, 29

Some Relations between Structure Factors

BY R. K. BULLOUGH AND D. W. J. CRUICKSHANK
School of Chemistry, The University, Leeds 2, England

(*Received* 30 *September* 1954 *and in revised form* 19 *October* 1954)

For a centrosymmetric structure of all like atoms, a series of relations between structure factors is derived. The relationship of these results to the Hauptman & Karle statistical formulae for structure-factor sign determination is indicated; but an important difference in the statistical weight of one formula leads to a relation, recently given also by Cochran, for the signs and magnitudes of certain structure factors.

Much attention is focused at the present time on the application of statistical methods to the derivation of relationships between structure factors. Some of these relationships, or their equivalents, can, however, be derived by direct trigonometrical manipulation when the structure consists of all like atoms. For small departures of the atomic scattering factors from their mean, the relationships remain statistically true for a structure of unlike atoms. In this note a set of relations similar in form to those derived by Hauptman & Karle (1953, 1954) will be derived trigonometrically.

In $P\bar{1}$ the structure factor $F_{\mathbf{h}}$ is given by

$$F_{\mathbf{h}} = 2\sum_{j=1}^{N/2} f_{j\mathbf{h}} \cos(2\pi \mathbf{h}.\mathbf{x}_j) ,$$

where $\mathbf{h}.\mathbf{x}_j = hx_j+ky_j+lz_j$.

A normalized structure factor $E_{\mathbf{h}}$ may then be defined by

$$E_{\mathbf{h}} = F_{\mathbf{h}} \Big/ \left(\sum_{j=1}^{N} f_{j\mathbf{h}}^2\right)^{\frac{1}{2}} .$$

When all the atoms in the cell are of like kind, in $P\bar{1}$,

$$E_{\mathbf{h}} = \frac{2}{N^{\frac{1}{2}}} \sum_{j=1}^{N/2} \cos(2\pi \mathbf{h}.\mathbf{x}_j) .$$

Hence

$$E_{\mathbf{L}}^2 = \frac{4}{N} \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} \cos(2\pi \mathbf{L}.\mathbf{x}_i) \cos(2\pi \mathbf{L}.\mathbf{x}_j) ,$$

and therefore

$$N^{\frac{1}{2}}(E_{\mathbf{L}}^2-1) = E_{2\mathbf{L}} + \frac{8}{N^{\frac{1}{2}}} S_{\mathbf{L}} , \qquad [\mathrm{A}]$$

where

$$S_{\mathbf{L}} = \sum_{i>j} \cos(2\pi \mathbf{L}.\mathbf{x}_i) \cos(2\pi \mathbf{L}.\mathbf{x}_j) .$$

[A] has been given in terms of $F_{\mathbf{h}}/f_{\mathbf{h}}$ by Cochran & Woolfson (1954). $(E_{\mathbf{L}}^2-1)$ is a sharpened Patterson coefficient which [A] shows to be composed of contributions from vector peaks relating to vectors through the centre of symmetry via $E_{2\mathbf{L}}$, and to the remaining vectors via $S_{\mathbf{L}}$.

Hughes (1953) has derived Sayre's (1952) relation in terms of unitary structure factors. In terms of normalized structure factors this relation is

$$\langle E_{\mathbf{h}_1} E_{\mathbf{h}_2} \rangle = \frac{1}{N^{\frac{1}{2}}} E_{\mathbf{L}} , \qquad [\mathrm{B}]$$
$$\mathbf{h}_1+\mathbf{h}_2=\mathbf{L}$$

where the left-hand side is the arithmetical mean of all products $E_{\mathbf{h}_1}E_{\mathbf{h}_2}$, formed subject to the condition $\mathbf{h}_1+\mathbf{h}_2 = \mathbf{L}$.

Hughes's method may be extended to derive relationships between intensities. By [A]

$$N(E_{\mathbf{h}_1}^2-1)(E_{\mathbf{h}_2}^2-1) = E_{2\mathbf{h}_1}E_{2\mathbf{h}_2} + \frac{8}{N^{\frac{1}{2}}}(E_{2\mathbf{h}_1}S_{\mathbf{h}_2}+E_{2\mathbf{h}_2}S_{\mathbf{h}_1}) + \frac{64}{N} S_{\mathbf{h}_1}S_{\mathbf{h}_2} ,$$

and therefore

$$N\langle(E_{\mathbf{h}_1}^2-1)(E_{\mathbf{h}_2}^2-1)\rangle = \langle E_{2\mathbf{h}_1}E_{2\mathbf{h}_2}\rangle + \frac{8}{N^{\frac{1}{2}}}(\langle E_{2\mathbf{h}_1}S_{\mathbf{h}_2}\rangle + \langle E_{2\mathbf{h}_2}S_{\mathbf{h}_1}\rangle) + \frac{64}{N}\langle S_{\mathbf{h}_1}S_{\mathbf{h}_2}\rangle , \qquad (1)$$

where the means are formed subject to $2\mathbf{h}_1+2\mathbf{h}_2=2\mathbf{L}$.