

constructed according to the general designs suggested by Lipson & Beevers (1936), Beevers & Lipson (1952) or Patterson & Tunell (1942).

Table 2 compares the numerical values of 18 structure factors as computed with strips accurate to 0.01 and to 0.001. The parameters are again those given in Table 1, and the formulas for  $F(0kl)$  and  $F(hk0)$  with  $k+l$  odd are given by equations (3) and (4). Columns *B* and *C* compare directly the approximate numerical values derived with the small set of strips with the exact values computed using the large set for parameters accurate to three places. In view of the anticipated discrepancies at larger indices, the quality of the agreement is rather surprising. Even for the planes (630), (830) and (047) the errors need not cause concern save in the final stages of the parameter-refining process. The only logical explanation for this unexpectedly good agreement at the higher indices is that the errors in the trigonometric products for the

various atoms, being random in sign and magnitude, tend to cancel each other on the average. For this reason the small set of strips may have a special value in solving complex structures involving many parameters. The lack of significant differences between the values in columns *A* and *B* demonstrates that in the earlier stages of parameter refinement one may assume the constancy of  $f_c/f_0$  and  $f_N/f_0$  with impunity.

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## The Meaning of the Average of $|F|^2$ for Large Values of the Interplanar Spacing\*

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It is shown that A. J. C. Wilson's equation,  $\langle I \rangle = \Sigma f^2$ , is valid only if  $d(hkl)$  is smaller than the smallest interatomic distance in the crystal. The correct equation for  $\langle I \rangle$  for use at large  $d$ 's is derived. It is shown that the equation,  $\langle I \rangle = \Sigma F_g^2$ , where  $F_g$  is the scattering power of a glob of atoms, is nearly correct for  $d$ 's larger than twice the shortest interatomic distance and smaller than the shortest distance between centers of globs. This last statement is most nearly true for globs that consist of 'spherical tops of scattering matter', i.e. whose second moment of scattering is the same for all directions.

### Introduction

In 1942, Wilson (1942) announced the discovery of a relation between the average of the squared magnitudes of the structure factors of a crystal and the atomic scattering factors. This relationship has the form:

$$\langle I \rangle = \sum_{j=1}^N f_j^2(s). \quad (1)$$

In (1),  $\langle I \rangle$  is the average value of  $|F(hkl)|^2$  for all values of  $h$ ,  $k$  and  $l$  for which  $s = 1/d(hkl)$  lies between  $s$  and  $s+ds$ ,  $N$  is the number of atoms in one unit cell of the crystal and  $f_j(s)$  is the scattering factor of the  $j$ th atom. In a later paper Wilson (1949) pointed out that in practical cases relation (1) is not valid at small values of  $s$  (large values of  $d(hkl)$ ) and suggested a limiting value of  $s$  beyond which (1) could be safely

applied. In the present paper, the interpretation of  $\langle I \rangle$  is discussed for the small values of  $s$  which can occur in the data from crystals with large unit cells.

In the following paragraphs, the exact equation corresponding to (1) will be derived and will be found to contain additional terms which become larger as the product  $sr_{ij}$  decreases (where  $r_{ij}$  is the distance between the  $i$ th and  $j$ th atoms), but which are unimportant for large values of  $sr_{ij}$ . It will then be shown—qualitatively—that equation (1) is generally valid only if the minimum value of  $sr_{ij}$  is unity. Consequently, equation (1) is useful only if, for each of the structure factors used in the averaging,  $d(hkl)$  is less than about 1.5 Å for organic crystals, or about 2 Å for most others; for larger values of  $d(hkl)$  equation (1) can be quite inaccurate and is therefore useless. *In particular, most crystalline proteins give diffraction effects only for  $d(hkl)$  greater than 1.5 Å and data from such crystals should never be interpreted by the use of equation (1).*

\* Contribution No. 1 from the Protein Structure Project.

Having shown that equation (1) is not even approximately true for small values of  $s$ , an interpretation of  $\langle I \rangle$  under these conditions will be presented.

### Derivation of the equation for $\langle I \rangle$

The structure factor  $F(\mathbf{s}) = F(hkl)$  of a crystal can be related to the coordinates  $x_j, y_j, z_j$  of the  $N$  atoms in a unit cell by the formula:

$$F(hkl) = \sum_{j=1}^N f_j(hkl) \exp [2\pi i (hx_j + ky_j + lz_j)], \quad (2)$$

or, in vector notation:

$$F(\mathbf{s}) = \sum_{j=1}^N f_j(s) \exp [2\pi i \mathbf{s} \cdot \mathbf{r}_j], \quad (3)$$

where

$$\mathbf{s} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

and

$$\mathbf{r}_j = x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}$$

with  $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$  the vector triple reciprocal to  $\mathbf{a}, \mathbf{b}, \mathbf{c}$  which in turn define the unit cell of the crystal. In (3),  $s = |\mathbf{s}|$  and  $f_j(s)$  is written instead of  $f_j(\mathbf{s})$  to indicate that the scattering power of an atom is assumed to be spherically symmetrical.

Let  $|F(\mathbf{s})|^2$  be written  $I(\mathbf{s})$ . Then:

$$I(\mathbf{s}) = \sum_{j=1}^N f_j^2(s) + \sum_{j \neq j'} \sum_{j'} f_j(s) f_{j'}(s) \exp [2\pi i \mathbf{s} \cdot (\mathbf{r}_j - \mathbf{r}_{j'})]. \quad (4)$$

The value of  $\langle I \rangle$  is obtained by averaging all the values of  $I(\mathbf{s})$  for which  $s$  lies between  $s$  and  $s + ds$ . Obviously, the terms in the expression for  $I(\mathbf{s})$  which do not depend on the direction of  $\mathbf{s}$  are not affected by the averaging process, but the others must be considered more carefully. The factor of the form  $\exp [2\pi i \mathbf{s} \cdot (\mathbf{r}_j - \mathbf{r}_{j'})]$  which occurs in each term of the double sum on the right of (4) has an average equal to  $(\sin 2\pi s r_{jj'}) / 2\pi s r_{jj'}$ , if all directions of  $\mathbf{s}$  are allowed. Here,  $r_{jj'} = |\mathbf{r}_j - \mathbf{r}_{j'}|$ . Unfortunately, only those directions of  $\mathbf{s}$  are allowed which correspond to integral values of  $h, k, l$  in  $\mathbf{s} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ ; however, if  $s$  is larger than twice the largest of  $|\mathbf{a}^*|, |\mathbf{b}^*|, |\mathbf{c}^*|$ , there will, in practical cases, be enough of these values to approximate a continuous distribution of directions for  $\mathbf{s}$ . With this assumption, then:

$$\langle I \rangle = \sum_j f_j^2(s) + \sum_{j \neq j'} \sum_{j'} f_j(s) f_{j'}(s) \frac{\sin 2\pi s r_{jj'}}{2\pi s r_{jj'}}. \quad (5)$$

The double sum on the right of (5) obviously becomes small as  $s$  increases, so that, if  $s$  is large enough, (5) becomes identical with (1). On the other hand, if  $s r_{jj'}$  is less than 0.5, the corresponding term in the double sum is positive and becomes larger as  $s$  decreases. Clearly, then, equation (1) is almost surely inaccurate, if  $s r_{jj'} < 0.5$  for any appreciable number of atom pairs in the crystal. It would be expected, and experience shows, that if  $s r_{jj'}$  is greater than unity

for all atom pairs, then equation (1) is sufficiently exact for practical purposes. For instance, in organic substances there are many bonds between neighboring atoms of length about 1.5 Å; in consequence, equation (1) can be used only for the part of the diffraction pattern with  $s > \frac{2}{3} \text{Å}^{-1}$ , i.e. with  $d(hkl) < 1.5 \text{Å}$ . This statement is equally true of proteins, the crystals of which rarely, if ever, produce diffraction effects corresponding to  $d(hkl) < 1.5 \text{Å}$ ; the application of equation (1) to the data from protein crystals is, therefore, always incorrect.

### The radial distribution function

A completely proper use of the values of  $\langle I \rangle$  is provided by the well known radial distribution function. This function,  $D(r)dr$ , is the total number of pairs of particles in the crystal for which the interparticle distance lies between  $r$  and  $r + dr$ . For instance, if the unit cell of a crystal contains two point atoms of scattering power 3 and 2, respectively, separated by 1 Å, the curve of  $D(r)$  against  $r$  will show sharp maxima at  $r = 0$  and  $r = 1 \text{Å}$  with weights of  $3^2 + 2^2 = 13$  and  $2 \times 3 + 3 \times 2 = 12$ , respectively (and at other values of  $r$  corresponding to the separations between atoms in different cells). This function can be calculated from  $\langle I \rangle$  by means of the formula:

$$D(r) = 8\pi r \int_0^{\infty} s \langle I \rangle \sin 2\pi s r ds. \quad (6)$$

This is a well known result (Warren & Gingrich, 1934) and need not be discussed at length in this article; it seems sufficient to point out that valuable information concerning possible structures can be obtained in this way directly from the intensity data.

### The concept of 'globs'

Another way of interpreting the values of  $\langle I \rangle$  is based on the use of 'globs'. A glob is a group of atoms in the crystal which can be chosen in various ways depending on the problem at hand. Let  $F_g(\mathbf{s})$  be the scattering factor of the  $g$ th glob in the unit cell. The positions of its atoms are most conveniently defined by vectors  $\mathbf{r}_{gt}$  which are the distances from the centroid of scattering of the  $g$ th glob to the  $t$ th atom of that same glob. Let  $\mathbf{r}_g$  be the position vector of the centroid of scattering of the glob. Then, if the atom  $j$  of the crystal is also the atom  $gt$ , we have  $\mathbf{r}_j = \mathbf{r}_g + \mathbf{r}_{gt}$ .

In these terms:

$$F(\mathbf{s}) = \sum_{g=1}^G F_g(\mathbf{s}) \exp [2\pi i \mathbf{s} \cdot \mathbf{r}_g], \quad (7)$$

where

$$F_g(\mathbf{s}) = \sum_{t=1}^{N_g} f_{gt}(s) \exp [2\pi i \mathbf{s} \cdot \mathbf{r}_{gt}]. \quad (8)$$

Here  $G$  is the number of globs in the unit cell of the crystal and  $N_g$  is the number of atoms in the  $g$ th glob. In these terms,  $I(\mathbf{s}) = |F(\mathbf{s})|^2$  can be written:

$$I(\mathbf{s}) = \sum_g |F_g(\mathbf{s})|^2 + \sum_{g \neq g'} \sum_{g'} F_g(\mathbf{s}) F_{g'}^*(\mathbf{s}) \times \exp [2\pi i \mathbf{s} \cdot (\mathbf{r}_g - \mathbf{r}_{g'})]. \quad (9)$$

The double sum in (9) can be rewritten in the form

$$\sum_j \sum_{j'} f_j(s) f_{j'}(s) \exp [2\pi i \mathbf{s} \cdot (\mathbf{r}_j - \mathbf{r}_{j'})]$$

if it is understood that  $j$  and  $j'$  refer to atoms in different globs. It is now possible to average (9) over all directions of  $\mathbf{s}$ , so as to obtain:

$$\langle I \rangle = \sum_g \overline{|F_g(\mathbf{s})|^2} + \sum_j \sum_{j'} f_j(s) f_{j'}(s) \frac{\sin 2\pi s r_{jj'}}{2\pi s r_{jj'}}, \quad (10)$$

where, again,  $j$  and  $j'$  refer to atoms in different globs. The number of terms in the double sum of (10) which contain small values of  $r_{jj'}$  is much smaller than the corresponding number of terms in (5), so that, in practice, this double sum is unimportant for much smaller values of  $s$  and it is possible to write

$$\langle I \rangle = \sum_g \overline{|F_g(\mathbf{s})|^2} \quad (11)$$

as a good approximation for considerably smaller values of  $s$  than those for which (1) is valid.

Suppose, for example, that a crystal has a large unit cell containing a large organic molecule consisting of several known radicals joined together into an unknown configuration. These radicals could be considered as globs, and equation (11) used, in order to verify the presence of these radicals in the structure and to determine the absolute intensity scale in a range of  $d(hkl)$  smaller than that in which (1) is applicable.

### Spherical globs

If the glob scattering factor  $F_g(\mathbf{s})$  is independent of the direction of  $\mathbf{s}$ , equation (11) can be given a still greater range of validity, for then the process of averaging equation (9) over all directions of  $\mathbf{s}$  can be done, without rewriting the double sum, to give directly:

$$\langle I \rangle = \sum_g F_g^2(s) + \sum_{g \neq g'} \sum_{g'} F_g(s) F_{g'}(s) \frac{\sin 2\pi s r_{gg'}}{2\pi s r_{gg'}}. \quad (12)$$

In (12),  $F_g^2(s)$  is written instead of  $\overline{|F_g(\mathbf{s})|^2}$ , because  $F_g(s)$  is independent of direction and is therefore a real number unaffected by the averaging process. It is seen that the double sum consists only of terms containing  $r_{gg'}$  and that it will, therefore, be unimportant for values of  $s r_{gg'} > 1$ . Consequently, in the range of  $s$  such that  $d(hkl)$  is smaller than the smallest distance between glob centers, we have

$$\langle I \rangle = \sum_g F_g^2(s) \quad (13)$$

and the globs themselves could be used as scattering elements in the theory of structure determination, just as atoms are used at present. Of course, an atomic grouping can never be strictly spherical, but it is sur-

prising how far from spherical a glob can be and still produce essentially spherical diffraction effects over wide ranges of  $s = 1/d(hkl)$ .

The conditions under which a glob produces spherical diffraction effects will now be investigated. Let (8) be expanded as a power series, thus:

$$\begin{aligned} F_g(\mathbf{s}) &= \sum_{t=1}^N f_t(s) \exp [2\pi i \mathbf{s} \cdot \mathbf{r}_t] \\ &= \sum_{t=1}^N f_t(s) \sum_{n=0}^{\infty} \left(\frac{1}{n!}\right) (2\pi i \mathbf{s} \cdot \mathbf{r}_t)^n \\ &= \sum_{n=0}^{\infty} \frac{(2\pi i)^n}{n!} \sum_{t=1}^N f_t(s) (\mathbf{s} \cdot \mathbf{r}_t)^n \\ &= \sum_{t=1}^N f_t(s) + 2\pi i \mathbf{s} \cdot \left[ \sum_{t=1}^N f_t(s) \mathbf{r}_t \right] + \frac{(2\pi i)^2}{2} \sum_{t=1}^N f_t(s) (\mathbf{s} \cdot \mathbf{r}_t)^2 + \\ &\quad \text{higher terms.} \end{aligned} \quad (14)$$

(The subscript  $g$  has been dropped on the right side of (14) since no ambiguity is possible.) The first term in the expansion is independent of the direction of  $\mathbf{s}$ , because atoms are sufficiently spherical, and the second term vanishes, because the origin of the vectors  $\mathbf{r}_t$  is at the glob's centroid of scattering. The third term is independent of the direction of  $\mathbf{s}$ , if the glob is a spherical top, i.e. if its 'second moment of scattering' is constant for all directions of  $\mathbf{s}$ . In this case,

$$\sum_{t=1}^N f_t(s) (\mathbf{s} \cdot \mathbf{r}_t)^2 = \frac{1}{3} s^2 \sum_{t=1}^N f_t(s) r_t^2. \quad (15)$$

The higher terms are small, unless  $\mathbf{s} \cdot \mathbf{r}_t$  is large; indeed, if the glob has a center of symmetry, all the terms with  $n$  odd vanish. Consequently, if the second moment of scattering is zero, i.e. for 'spherical glob', it is possible to write (14) as follows:

$$F_g(s) = \sum_{t=1}^N f_t(s) - \frac{1}{3} (2\pi s)^2 \sum_{t=1}^N f_t(s) r_t^2 + \text{higher terms.} \quad (16)$$

It is interesting that the first two terms of (16) are in agreement with the approximation:

$$F_g(s) = \sum_{t=1}^N f_t(s) \frac{\sin 2\pi s r_t}{2\pi s r_t}. \quad (17)$$

Formula (17) would be exact, if each atom in the glob were smeared out over the surface of a spherical shell of radius equal to the atom's distance from the glob center.

How well does the approximate formula (17) hold in practical cases? Two examples are presented below. The glob in the first example is somewhat extreme in that its distribution of scattering material is about as unsymmetrical as is possible for a spherical top. It consists of four point scatterers of relative powers 1, 2, 3 and 4 at the corners of a small distorted tetrahedron centered at the lattice points. The Cartesian coordinates of these scattering points are given in Table 1; also given in Table 1 are the trimetric coor-

Table 1. *Coordinates of scatterers in a four-point spherical top*

Scattering power <i>f</i>	Cartesian coordinates (Å)			Trimetric coordinates*			Radius (Å)† <i>r<sub>j</sub></i>
	<i>x<sub>c</sub></i>	<i>y<sub>c</sub></i>	<i>z<sub>c</sub></i>	<i>x = x<sub>c</sub>/a<sub>0</sub></i>	<i>y = y<sub>c</sub>/b<sub>0</sub></i>	<i>z = z<sub>c</sub>/c<sub>0</sub></i>	
1	0	$0.7 \times \sqrt{2}$	$0.2 \times \sqrt{70}$	0.00	0.07	0.14	1.944
2	0	$0.7 \times \sqrt{2}$	$-0.1 \times \sqrt{70}$	0.00	0.07	-0.07	1.296
3	$-0.4 \times \sqrt{5}$	$-0.3 \times \sqrt{2}$	0	-0.08	-0.03	0.00	0.990
4	$0.3 \times \sqrt{5}$	$-0.3 \times \sqrt{2}$	0	0.06	-0.03	0.00	0.794

\* Referred to an orthorhombic cell with

$$a_0 = 5\sqrt{5}, b_0 = 10\sqrt{2}, c_0 = (10/7)\sqrt{70} \text{ \AA}.$$

† The radius of gyration of the glob is 1.122 Å.

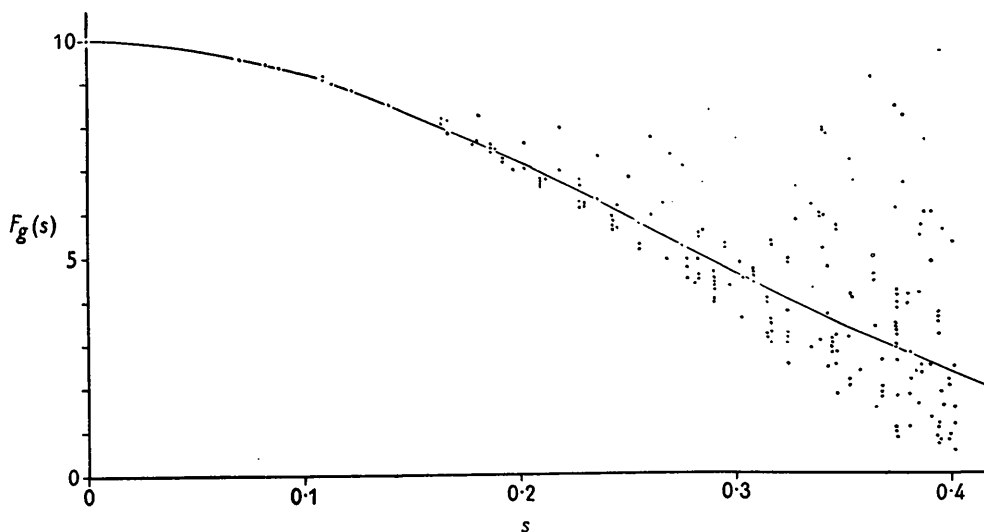


Fig. 1. Comparison of  $|F|$  (dots) with equation (17) (curve) for the distorted tetrahedron.

ordinates of these points when referred to an orthorhombic lattice of axial lengths:  $a_0 = 5\sqrt{5}$ ,  $b_0 = 10\sqrt{2}$ ,  $c_0 = (10/7)\sqrt{70}$  Å.

The structure described in Table 1 is triclinic, but the orthorhombic lattice was chosen for computational convenience.

Structure factors were computed for this hypothetical crystal structure by means of equation (2); their magnitudes are plotted as points in Fig. 1. Approximate structure factors were also computed by means of equation (17), since for this case equation (7) becomes  $F(\mathbf{s}) = F_g(s)$ . The values of  $F_g(s)$  are plotted as a smooth curve in Fig. 1. It is seen that the points lie quite close to the curve for values of  $s$  up to 0.26, but then begin to diverge seriously. The radius of gyration,  $R$ , of the glob is 1.122 Å, so that for  $sR < 0.3$ , the approximation represented by formula (17) is adequate, even in this extreme case.

The second example is that of a regular octahedron of scattering points centered at the origin of a simple cubic lattice. The six vertices of this octahedron are at  $0, 0, \pm \frac{1}{2}\sqrt{3}$ ;  $0, \pm \frac{1}{2}\sqrt{3}, 0$ ;  $\pm \frac{1}{2}\sqrt{3}, 0, 0$  in trimetric coordinates. If the length of one unit cell edge is 25 Å, the octahedron will be 1.77 Å on an edge—a possible interatomic distance. (This compares with the following

lengths of the edges of the tetrahedron of the first example: (1)-(2), 2.51 Å; (1)-(3), 2.36 Å; (1)-(4), 2.29 Å; (2)-(3), 1.87 Å; (2)-(4), 1.78 Å; (3)-(4), 1.57 Å.) Fig. 2 presents a plot of the values of  $|F|$  for this crystal, together with a curve showing the glob approximation to  $F$ . It is seen that in this case the approximation is excellent for values of  $s$  up to at least 0.3, i.e. for values of  $sR$  less than 0.4 since  $R = 1.25$  Å.

Having shown that the structure factors of spherical tops of scattering matter produce essentially spherically symmetrical scattering effects, it is, therefore, appropriate to use equation (13) in part of the range where Wilson's equation (1) fails. The two examples treated in the last few paragraphs can be used to show, qualitatively, the range in which equation (13) can be used.

Figs. 3 and 4 are plots of  $\langle I \rangle$  calculated, respectively, from the structure factors of the tetrahedron of Fig. 1 and the octahedron of Fig. 2. (The values of  $\langle I \rangle$  are shown by small circles.) The approximation of equation (17) for  $F_g(s)$  was used to calculate  $F_g^2(s)$  which is plotted on each of Figs. 3 and 4 as a full line; the approximation of equation (1) is plotted as a broken line. It is immediately obvious that equation (1) is valid for  $sr_{ij} \geq 1$ , while equation (17) gives good

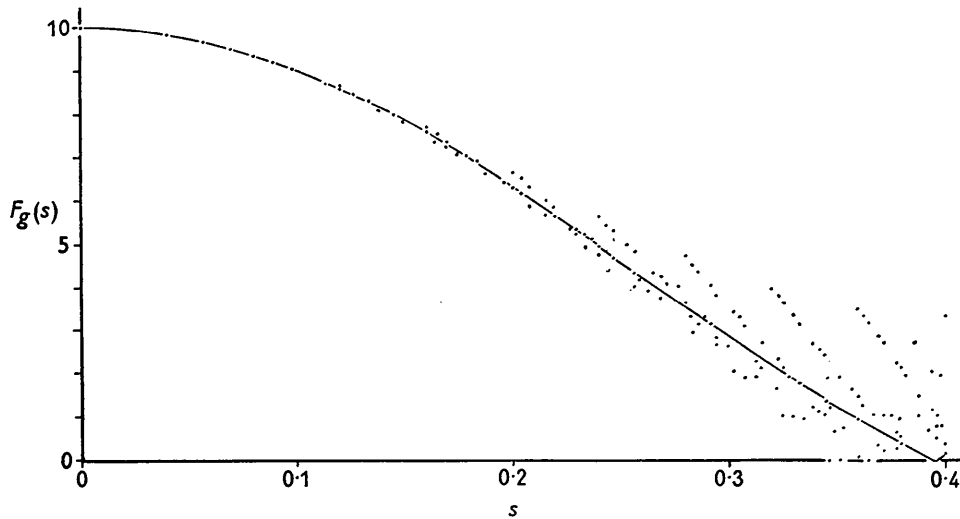


Fig. 2. Comparison of  $|F|$  (dots) with equation (17) (curve) for the regular octahedron.

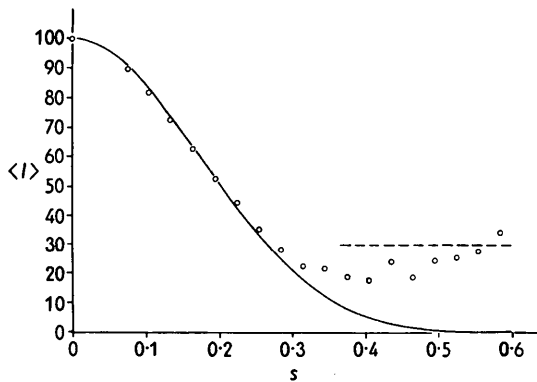


Fig. 3.

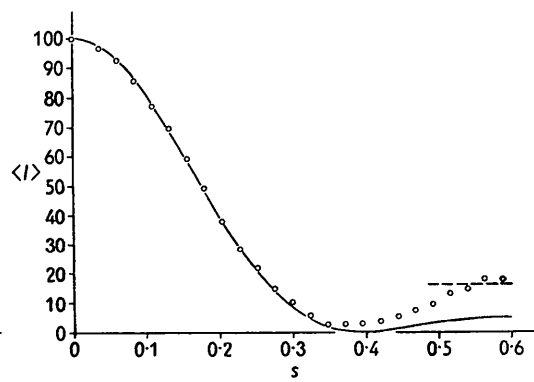


Fig. 4.

Fig. 3. Comparison of  $\langle I \rangle$  (small circles) with the square of equation (17) (full curve) and with equation (1) (broken line) for the distorted tetrahedron.

Fig. 4. Comparison of  $\langle I \rangle$  (small circles) with the square of equation (17) (full curve) and with equation (1) (broken line) for the regular octahedron.

results if  $sr_{ij} \leq \frac{1}{2}$ ; in the intervening region the values of  $\langle I \rangle$  trend smoothly from one approximation to the other. (Of course, at all values of  $s$ , equation (5) is valid.)

If, in the examples just treated, there had been more than one glob per unit cell, the approximation of equations (12) or (13) would have become poor for values of  $sr_{gg'} \leq 1$ . In other words, these approximations are useful in the range of  $d(hkl)$  between the smallest interglob distance and twice the smallest interatomic distance.

### Discussion

A common device in the treatment of X-ray diffraction data, before using them for structure determination, is that of dividing the  $|F(s)|^2$ 's by the quantity  $(\sum f_j(s))^2$ . This results in numbers which are approximately the  $|F(s)|^2$ 's to be expected from a crystal

composed of point atoms, instead of real atoms with electron clouds having some extent in space; the point atoms have the positions of the atoms in the real crystal (and also their thermal motions, unless corrections for this have been included in the values of  $f_j(s)$ ). If all the atoms in a crystal are (nearly) the same,  $(\sum f_j(s))^2$  can be written  $N^2 f^2(s)$ , which is the same as  $N \sum f_j^2(s)$  in this case. Therefore, in the range of validity of equation (1), this expression is equal to  $N \langle I \rangle$ . (Indeed, the use of this equality automatically corrects for the thermal motion of the atoms, if this is the same for all atoms.) Consequently, if the experimental values of  $|F(s)|^2$  are divided by  $N \langle I \rangle$  in the range  $d(hkl) \leq r_{ij}$ , the resulting numbers are the  $|F(s)|^2$ 's of the point-atom crystal. Furthermore, this process can be used to place the diffraction data from the crystal on an absolute scale, as pointed out by Wilson (1942).

In a similar way, the  $|F(s)|^2$ 's of a crystal containing

scattering points at the positions of glob centers can be derived from the  $|F(\mathbf{s})|^2$ 's of the real crystal through dividing by  $G\langle I \rangle$  in the range  $2r_{ij} < d(hkl) < r_{gg}$ , provided that the globs in the crystal are 'spherical' and all alike. This raises the question of the existence of spherical globs in crystals.

One can say at once that the glob concept is useful only in connection with crystals with large unit cells as there must be a large number of interplanar spacings greater than 3 Å. The unit cells of such crystals contain a large number of atoms,\* which can be grouped into globs in many different ways. If, in interpreting the values of  $\langle I \rangle$ , it is assumed that the glob factors are spherical ( $F_g(\mathbf{s}) = F_g(s)$ ), the globs themselves must be (nearly) spherical globs and correspond to only certain ways of dividing the atoms in the cell into groups. It is probable that some structures do not provide any way of assigning the atoms to groups so as to make spherical globs, but it seems likely that many complex structures can provide nearly spherical globs by some method of subdivision. The assumption that  $\langle I \rangle = NF_g^2(s)$  corresponds to selecting a method of distributing the atoms into spherical globs, all with the same sets of interatomic distances.

When the structure of a crystal can be thought of as a set of similar globs in various positions and with different orientations, each of the structure factors is very probably near the value

$$F(s) = \sum_{j=1}^G \overline{F_g(\mathbf{s})} \exp [2\pi i s \cdot r_g] \quad (18)$$

\* In organic crystals, the number of reflections with  $d > 3$  Å is about ten times the number of atoms in the unit cell, not counting hydrogen.

obtained from formula (7) by replacing each  $F_g(\mathbf{s})$  by its average over all orientations. This statement is true, even if the globs are quite far from being spherical, provided enough different orientations of the globs are present. In such a case:

$$\langle I \rangle = \sum_{g=1}^N \overline{(F_g(\mathbf{s}))^2} = G \overline{(F_g(\mathbf{s}))^2}, \quad (19)$$

which is almost the same as (11), because

$$\frac{\overline{\sin 2\pi s r_{ij'}}}{2\pi s r_{ij'}} = \frac{\sin 2\pi s r_j}{2\pi s r_j} \cdot \frac{\sin 2\pi s r_{j'}}{2\pi s r_{j'}}, \quad (20)$$

where the bar over the left hand term indicates averaging  $r_{ij'}$  over all directions of  $\mathbf{r}_i$  and  $\mathbf{r}_{j'}$ . Consequently, a satisfactory approximation to a point-glob crystal is obtained by dividing the  $|F(\mathbf{s})|^2$ 's by  $G\langle I \rangle$  in this case also, which can occur quite frequently in complicated crystals.

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## The Structure of Diphenylene Naphthacene

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The unit cell of diphenylene naphthacene is monoclinic, with  $a = 11.0 \pm 0.05$ ,  $b = 5.15 \pm 0.03$ ,  $c = 19.6 \pm 0.10$  Å,  $\beta = 126^\circ$ . The space group is  $P2_1/c$ , and in the unit cell are two molecules, each lying on a centre of symmetry. The structure was solved by optical-transform methods, and the atomic positions were found with the aid of the (010) and (100) Fourier projections.

### Introduction

This compound is one of a number investigated largely by optical diffraction methods (Hanson, Taylor & Lipson, 1952). The procedure by which the approximate structure was determined is discussed elsewhere (Hanson, Lipson & Taylor, 1953), and will not be considered here.

### Unit cell and space group

The sample supplied consisted of a number of lath-like, blue, opaque crystals; although these were extremely thin, and showed a slight tendency to bend, no difficulty was experienced in selecting single crystals suitable for X-ray examination.