4. Concluding remarks

It is safe to say that the preponderance of our present knowledge about the electron-microscope contrast behavior of defects in crystals was obtained using diffraction equations based upon the column approximation. However, the use of these equations to describe defect contrast under high-resolution conditions is dangerous. In this paper we have demonstrated two ways (image shifting and fringing) in which the column-approximation equations fail to predict contrast for point and line defects. However, we have not discussed the visibility of the fringing. Our feeling is that if it can be resolved, it will most probably be visible in weak-beam images of point defects and very small precipitates. Of course, this question will only be answered by the experimentalist. In a future paper we will discuss the effect of the column approximation on the calculation of images of planar defects.

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Symmetry- and Composition-Dependent Cumulative Distributions of the Normalized Structure Amplitude for Use in Intensity Statistics

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Abstract

Centric and acentric cumulative distribution functions of the normalized structure amplitude, which explicitly account for the presence of outstandingly heavy atoms in crystals of any symmetry, have been derived. These cumulative distributions can now be readily evaluated for all triclinic, monoclinic and orthorhombic space groups, with the exceptions of *Fdd*2 and *Fddd*, and thus constitute an extension of the commonly employed cumulative distributions based on the Wilson statistics. Expected discrepancies between the distributions derived in this work and the corresponding Wilson-type distributions are illustrated, and their symmetry and composition dependence is discussed in view of relevant applications to intensity statistics.

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Introduction

The known methods of intensity statistics, which are applicable to the resolution of space-group ambiguities, can be classified into (*A*) computation of an experimental average of a function of the structure amplitude and comparison of this average with its theoretical expectation values for the possible space groups, and (*B*) comparison of experimental and theoretical distributions of the normalized intensity or structure amplitude. Most existing methods of both classes are based on the Wilson (1949) statistics, according to which the structure amplitude from an equal-atom structure, with a large number of atoms in the unit cell, is normally distributed, the distribution parameters being different for the centrosymmetric and noncentro-

symmetric cases. The literature on this subject is quite extensive and much of it has recently been reviewed by Srinivasan & Parthasarathy (1976).

It is well known that tests based on the Wilson (1949) statistics [*e.g.* the $N(z)$ test (Howells, Phillips & Rogers, 1950); averages of $|E|$ and $|E^2-1|$ (Karle, 1976)] often give satisfactory results – even if the formal requirements of this statistics are not exactly observed. However, a difficulty such as, for example, the presence of an outstandingly heavy atom, may well lead to inconclusive or wrong results of such tests. An important development, within class *A* methods, has been made in the study of Foster & Hargreaves (1963*a*,*b*), who derived generalized moments of normalized intensity, which depend explicitly on the symmetry and composition of the crystal. The effect of disparity of atomic scattering powers on the intensity averages can thus be accounted for, and it has been demonstrated (*e.g.* Foster & Hargreaves, 1963*b*; Goldberg & Shmueli, 1971) that deviations of intensity moments, from their values predicted by the Wilson (1949) statistics, are correctly indicated by the generalized moment test. Foster & Hargreaves (1963*b*) evaluated the symmetry-dependent parts of the second and third moments of intensity for all triclinic, monoclinic and orthorhombic space groups (except *Fdd*2 and *Fddd*).

There appears to be no equivalent development within class *B* methods. The most popular of these is the $N(z)$ cumulative distribution test (Howells *et al.*, 1950) but, as mentioned above, it too may give misleading indications when outstandingly heavy atoms are present in the structure. It was therefore thought desirable to derive symmetry- and composition-dependent cumulative distributions of $|E|$ and to combine thereby the well known advantages of cumulative distributions over single expectation values with a generalized approach to intensity statistics, such as that of Foster & Hargreaves (1963*a*). The purpose of this paper is to derive and illustrate such cumulative distribution functions of the normalized structure amplitude, for the centric as well as acentric cases.

Derivation

We wish to find expressions for the fraction of $|E|$ values, not exceeding a given $|E'|$, and require that these cumulative distribution functions depend on the composition of the asymmetric unit, *i.e.* that disparity of atomic scattering powers be allowed for, and on the symmetry of the crystal. Suitable probability density functions, showing the required dependence, were first given by Karle & Hauptman (1953) and by Hauptman & Karle (1953*a*), for the centrosymmetric and noncentrosymmetric cases respectively, in terms of the structure amplitude $|F|$, atomic scattering factors and moments of trigonometrical structure factors, which depend on crystal symmetry. In what follows, we shall use the corresponding probability density functions for the normalized structure amplitude $|E|$ (*e.g.* Hauptman & Karle, 1953*b*; Srinivasan & Parthasarathy, 1976). These functions can be written as

$$P_c(|E|)=\left(\frac{2}{\pi}\right)^{1/2}\exp\left(-\frac{|E|^2}{2}\right)\times[1+A(\tfrac{1}{3}|E|^4-2|E|^2+1)+B(\tfrac{1}{15}|E|^6-|E|^4+3|E|^2-1)+\ldots], \quad (1)$$

and

$$P_a(|E|)=2|E|\exp(-|E|^2)[1+C(\tfrac{1}{2}|E|^4-2|E|^2+1)+D(\tfrac{1}{8}|E|^6-\tfrac{3}{2}|E|^4+3|E|^2-1)+\ldots]. \quad (2)$$

for the centric and acentric distributions respectively, where *A*, *B*, *C* and *D* are composition- and symmetry-dependent coefficients. All the above expansion terms will be retained in what follows. Explicit functional forms of these coefficients are given in the papers of Hauptman and Karle (see above). However, it appears more convenient for the present purpose to re-express these coefficients in terms of even moments of $|E|$, for which theoretical expressions are also available (Karle & Hauptman, 1953; Hauptman & Karle, 1953*a*; Foster & Hargreaves, 1963*a*) and which were numerically evaluated for a large range of space groups (Foster & Hargreaves, 1963*b*). Equations (1) and (2) can thus be transformed to a form which is suitable for use in intensity statistics. The integrals to be evaluated for this purpose are $\langle|E|^4\rangle_\alpha=\int_0^\infty |E|^4P_\alpha(|E|)\,\mathrm{d}|E|$ and $\langle|E|^6\rangle_\alpha=\int_0^\infty |E|^6\,P_\alpha(|E|)\,\mathrm{d}|E|$, where $\alpha=c$ and $\alpha=a$ refer to probability density functions (1) and (2) respectively. We thus have

$$A=(\langle|E|^4\rangle_c-3)/8, \quad (3)$$

$$B=(\langle|E|^6\rangle_c-15\langle|E|^4\rangle_c+30)/48, \quad (4)$$

$$C=(\langle|E|^4\rangle_a-2)/2, \quad (5)$$

$$D=(\langle|E|^6\rangle_a-9\langle|E|^4\rangle_a+12)/6. \quad (6)$$

Equation (1), with *A* and *B* given by (3) and (4) respectively, is equivalent to the corresponding expression for the probability density function of a centrosymmetric structure factor, given by Bertaut (1955).

It is readily seen, as expected, that equations (1) and (2) tend to the corresponding Wilson-type distributions, as the moments of $|E|$ tend to values expected from such distributions. Conversely, such values of $\langle|E|^4\rangle$ and $\langle|E|^6\rangle$ are approached as the number of (equal)

atoms in the asymmetric unit increases. Hence the symmetry- and composition-dependent terms in square brackets in (1) and (2) should be regarded as departures from the distributions which are based on the central limit theorem (Wilson, 1949, and references therein).

We can now evaluate the required cumulative distributions by integrating (1) and (2), using the coefficients A, B, C and D as given by (3), (4), (5) and (6) respectively. The integrations can be kept simple and concise results follow, when the polynomials in $|E|$ appearing in equations (1) and (2) are expressed in terms of Hermite polynomials,* $H_n(x)$. The relevant identities are

$$\tfrac{1}{3}|E|^4 - 2|E|^2 + 1 = \tfrac{1}{12}H_4\left(\frac{|E|}{\sqrt{2}}\right), \qquad (7)$$

and

$$\tfrac{1}{15}|E|^6 - |E|^4 + 3|E|^2 - 1 = \tfrac{1}{120}H_6\left(\frac{|E|}{\sqrt{2}}\right), \qquad (8)$$

to be used with (1), and

$$\tfrac{1}{2}|E|^5 - 2|E|^3 + |E| = \tfrac{1}{16}[\tfrac{1}{4}H_5(|E|) + H_3(|E|) - H_1(|E|)], \qquad (9)$$

and

$$\tfrac{1}{6}|E|^4 - \tfrac{3}{2}|E|^5 + 3|E|^3 - |E| = \tfrac{1}{96}[\tfrac{1}{8}H_2(|E|) + \tfrac{3}{4}H_5(|E|) - \tfrac{3}{2}H_3(|E|) + 3H_1(|E|)], \qquad (10)$$

to be employed with (2). The calculation is performed with the aid of the known definite integral

$$\int_0^x e^{-t^2}H_n(t)\,dt = H_{n-1}(0) - e^{-x^2}H_{n-1}(x) \qquad (11)$$

(*e.g.* Hochstrasser, 1970).

We thus obtain

$$N_c(|E'|) = \int_0^{|E'|} P_c(|E|)\,d|E| = \operatorname{erf}\left(\frac{|E'|}{\sqrt{2}}\right) - \frac{2}{\sqrt{\pi}}\exp\left(-\frac{|E'|^2}{2}\right) \times\left[\frac{A}{12}H_3\left(\frac{|E'|}{\sqrt{2}}\right) + \frac{B}{120}H_5\left(\frac{|E'|}{\sqrt{2}}\right)\right], \qquad (12)$$

and

$$N_a(|E'|) = \int_0^{E'} P_a(|E|)\,d|E| = 1 - \exp(-|E'|^2) + \sum_{n=0}^{3} a_n[H_{2n}(0) - \exp(-|E'|^2)H_{2n}(|E'|)], \qquad (13)$$

for the centric and acentric cumulative distribution functions of $|E'|$ respectively, where

$$a_0 = -\frac{C}{8} + \frac{D}{16}, \quad a_1 = \frac{C}{8} - \frac{D}{32}, \quad a_2 = \frac{C}{32} + \frac{D}{64}, \quad a_3 = \frac{D}{384},$$

and A, B, C and D are given by equations (3)–(6).

It may now be pointed out that the first term on the RHS of (12) and the first two terms on the RHS of (13) are just the centric and acentric cumulative distribution functions of $|E'|$ based on the Wilson (1949) statistics respectively.

Evaluation of cumulative distributions

The dependence of even moments of intensity on crystal symmetry and composition, as given by Karle & Hauptman (1953), Hauptman & Karle (1953*a*) and Foster & Hargreaves (1963*a*), requires an evaluation of the moments of the trigonometrical structure factor for each space group in question. The most extensive compilation of these quantities, published to date, has been given by Foster & Hargreaves (1963*b*) who have listed composition-dependent expressions for $\langle|F|^2\rangle$, $\langle|F|^4\rangle$ and $\langle|F|^6\rangle$ for all triclinic, monoclinic and orthorhombic space groups, except *Fdd*2 and *Fddd* which are anyway uniquely defined by their conditions for possible reflections.

Noting that $\langle|E|^4\rangle = \langle|F|^4\rangle/\langle|F|^2\rangle^2$ *etc.*, we can write, following Foster & Hargreaves (1963*b*),

$$\langle|E|^4\rangle = 3 + a\frac{S(4)}{S^2(2)}, \qquad (14)$$

$$\langle|E|^6\rangle = 15 + b\frac{S(4)}{S^2(2)} + c\frac{S(6)}{S^3(2)}, \qquad (15)$$

for centrosymmetric space groups, and

$$\langle|E|^4\rangle = 2 + a\frac{S(4)}{S^2(2)}, \qquad (16)$$

* A convenient transformation table is given by Abramovitz & Stegun (1970).

$$\langle |E|^6 \rangle = 6 + b\frac{S(4)}{S^2(2)} + c\frac{S(6)}{S^3(2)}, \qquad (17)$$

for noncentrosymmetric space groups, where

$$S(p) = \sum_{j=1}^{t} f_j^p, \qquad (18)$$

f_j being the scattering factor of the jth atom, t the number of atoms in the asymmetric unit, and a, b and c are symmetry-dependent coefficients, evaluated from Table 1 of a Foster & Hargreaves (1963*b*) and listed below according to the relevant point groups:

a	b	c	Point group
−1	−9	4	1
−1·5	−22·5	10	$\bar{1}$
−0·5	−4·5	1	2 or m
−0·75	−11·25	2·5	$2/m$
−0·25	−2·25	0·25	222
0·25	2·25	−2	$mm2$
0·375	5·625	−5	mmm.

The cumulative distributions $N_c(|E'|)$ and $N_a(|E'|)$ can now be explicitly evaluated for the above crystal symmetries. For example, $N_c(|E'|)$ for space group $P2_1/m$ is given by (12), with A and B defined by (3) and (4) which, in turn, depend on $\langle |E|^4 \rangle$ and $\langle |E|^6 \rangle$ as given by (14) and (15) and the fourth row of the above table.

We shall illustrate the effects of an outstandingly heavy atom and various crystal symmetries on the above distributions by means of a hypothetical and yet realistic example. Consider a crystal structure with 20 carbon atoms and one heavier atom in the asymmetric unit, and let this atom be taken, in turn, as chlorine, bromine and iodine. The composition-dependent terms can be approximately evaluated assuming that the ratio of two scattering factors, for the same diffraction vector, is independent of $\sin\theta/\lambda$. That is,

$$\frac{S(4)}{S^2(2)} = \frac{20f_c^4 + f_x^4}{(20f_c^2 + f_x^2)^2} = \frac{20 + \rho^4}{(20 + \rho^2)^2},$$

where $\rho = f_x/f_c \simeq Z_x/Z_c$ and Z is the atomic number.

Fig. 1(*a*) and (*b*) displays the centric $N_c(|E'|)$ and acentric $N_a(|E'|)$ distributions, given by (12) and (13) respectively, for $C_{20}I$ in the various symmetries listed above. In the case of $\bar{1}$ symmetry, the $N_c(|E'|)$ curve [Fig. 1(*a*)] lies closer to the acentric than to the centric Wilson-type distribution and may thus be useful in resolving $P1$ *vs* $P\bar{1}$ ambiguities. The result for $2/m$ [Fig. 1(*a*)], if it represented an experimental distribution, would be classified as inconclusive, while the *mmm* curve [Fig. 1(*a*)] does not differ greatly from the Wilson-type centric distribution. In the case of $C_{20}Br$, the only serious deviation appears to be that for the $\bar{1}$ symmetry while for $C_{20}Cl$, both the $N_c(|E'|)$ and $N_a(|E'|)$ distributions practically coincide with the corresponding Wilson-type distributions, for all symmetries considered. Qualitatively similar results, but with somewhat smaller deviations, were also obtained for a $C_{25}X$ asymmetric unit.

The above example suggests that the use of the $N_c(|E'|)$ distribution in actual statistical tests is likely to be of value, since the curves for $\bar{1}$ and $2/m$ symmetries fall *between* the centric and acentric Wilson-type $N(|E'|)$ curves and the generalized distribution derived here may thus be helpful in resolving corresponding space-group ambiguities. The deviations observed in the various $N_a(|E'|)$ distributions [Fig. 1(*b*)], in the monoclinic and triclinic symmetries, make these distributions look 'even more acentric' and hence practical tests with $N_a(|E'|)$ curves are likely to be important in the case of very heavy atoms or a particularly small number of light atoms in the asymmetric unit. In any case, equations (12) and (13) may serve as a useful extension of existing statistical tests which are routinely performed in the various programs for normalized structure amplitude calculation.

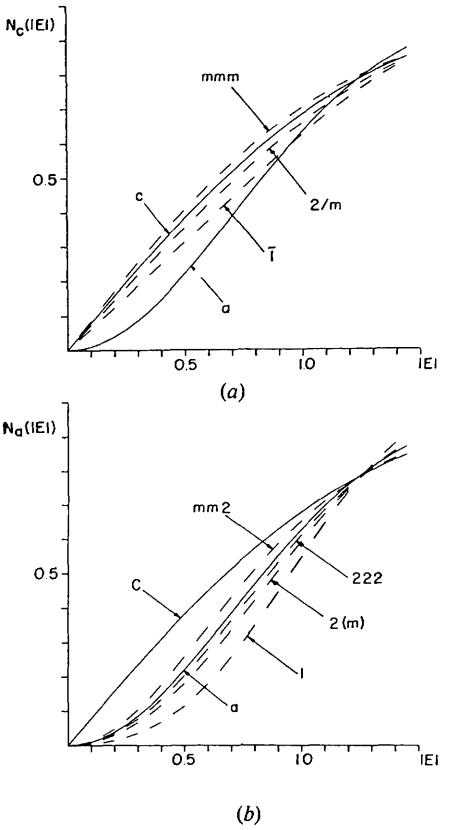

Fig. 1. Comparison of the cumulative distributions (12) and (13) (dashed lines) with the Wilson-type centric and acentric $N(|E'|)$ functions (solid lines) for $C_{20}I$. (*a*) $N_c(|E'|)$ for point groups 1, $2/m$ and *mmm*. (*b*) $n_a(|E'|)$ for point groups 1, 2 (or m), 222 and $mm2$.

It must be pointed out that the present results apply only to the case of atoms in general positions and, like most conventional statistical tests, they do not overcome the problems of possible hypersymmetry. In the case of light-atom hypersymmetric structures, use can be made of the cumulative distributions given by Lipson & Woolfson (1952) and Rogers & Wilson (1953) (*cf.* Goldberg & Shmueli, 1973), while for the case of outstandingly heavy atoms modified probability density functions and/or modified expressions for the higher moments of $|E|$ are required.

It should also be pointed out that the more extensive validity of the Wilson-type methods (more extensive than their underlying assumptions might lead one to expect) is probably due in part to the decrease of the correction terms in (14)–(17) with increasing symmetry. This is indicated by the above example and may account for numerous successful outcomes of $N(z)$ tests (Howells *et al.*, 1950) carried out with moderately heavy atoms.

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High-Resolution Diffuse X-ray Scattering Study from Nearly Perfect Silicon Single Crystals

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Abstract

High-resolution measurements of diffuse X-ray scattering (DXS) have been made at and above room temperature around 111, 333, 444 and 555 reciprocal lattice points (relps) using highly collimated Mo $K\alpha_1$ and Cu $K\alpha_1$ radiations with the specimen set in $(1, -1, 1)$ symmetrical Bragg geometry. The distribution of DXS intensity around different relps has shown that at temperatures up to at least 573 K the contribution of thermal DXS to the observed DXS is very small. This is apparently due to the high value of the Debye temperature (640 K) of silicon. A remarkable feature of these results is that for the same value of the scattering vector $|\mathbf{K}^*|$ the DXS intensity is different for the parallel and antiparallel orientations of $\mathbf{K}^*$ relative to $\mathbf{R}^*$. The amount of anisotropy varied from sample to sample and depended on the thermal history of the specimen. This and the other features show that the observed DXS is predominantly due to point defects and their aggregates. A typical size parameter for the aggregates is 3000 to 10 000 Å.

1. Introduction

Point defects, their aggregates and elastic thermal waves give diffuse X-ray scattering (DXS) from regions of reciprocal space close to the reciprocal-

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