

## The Probability Distribution of X-ray Intensities

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In a crystal without symmetry elements and containing a sufficiently large number of atoms the probability of the  $hkl$  reflexion having an intensity between  $I$  and  $I+dI$  is  $P(I) dI$ , where  $P(I) = \Sigma^{-1} \exp\{-I/\Sigma\}$ , and  $\Sigma$  is the sum of the squares of the scattering factors of the atoms. In a centrosymmetric crystal the probability of the structure amplitude of the  $hkl$  reflexion lying between  $F$  and  $F+dF$  is  $P(F) dF$ , where  $P(F) = (2\pi\Sigma)^{-\frac{1}{2}} \exp\{-F^2/2\Sigma\}$ , a result noticed empirically. In a centred crystal  $(k-1)/k$  of the reflexions are zero, and the remaining  $1/k$  of them are distributed like those of an uncentred crystal with parameter  $k\Sigma$ , where  $k$  is 4 for face-centring and 2 for end- or body-centring. Other symmetry elements do not produce important effects on the general reflexions, but may make a zone or line of intensities behave as if centred or centrosymmetric. The mean value of  $I$  is  $\Sigma$ , a fact that can be used to put relative intensities on an absolute basis. The mean values of  $|F|$  or  $I^2$  can also be used, but the mean value of  $I$  is the only one independent of the symmetry. The difference between the ratios of  $\langle |F|^2 \rangle$  to  $\langle I \rangle$  for centrosymmetric and non-centrosymmetric crystals may serve for the purely X-ray determination of a centre of symmetry.

Some years ago the writer suggested a method for the determination of absolute from relative intensities (Wilson, 1942), and as a natural extension endeavoured to determine the probability distribution function for X-ray intensities. When a paper on this subject was in an advanced stage, Hughes (1949) showed that a similar process\* was of use in connexion with the Harker-Kasper inequalities, and observed that, empirically, the values of the structure amplitude (for centrosymmetric crystals containing only atoms of similar scattering powers) have an approximately normal distribution about zero. The present paper contains a theoretical justification of Hughes's observation, and some discussion of the distribution functions for crystals with other symmetry elements. It was originally planned to include a comparison of observed and theoretical distributions, but this is now omitted in view of Hughes's work.

### 1. Introduction

In simple crystals containing only a few atoms per unit cell all the positions of the atoms are pretty well fixed by considerations such as charge, packing, and valency angles. In more complex crystals the positions of the atoms, although ultimately depending on the same factors, are in a sense random, and some conclusions about the intensities of X-ray reflexions can be established on statistical grounds. The structure amplitude of the  $hkl$  reflexion from a crystal containing  $N$  atoms per unit cell is given by

$$F = \sum_{j=1}^N f_j \exp\{2\pi i(hu_j + kv_j + lw_j)\}, \quad (1)$$

\* Harker (1948) also has discussed a process of obtaining absolute from relative intensities. The earliest suggestion, based on a somewhat different principle and rather difficult to put into practice, appears to be that of Hettich (1935) (Hughes, private communication).

where  $f_j$  is the scattering factor and  $u_j, v_j, w_j$  are the fractional co-ordinates of the  $j$ th atom. This may be represented graphically on a vector diagram as the resultant of  $N$  displacements of amounts  $f_j$  at angles  $\delta_j \equiv 2\pi(hu_j + kv_j + lw_j)$  to the  $x$  axis. The problem is to find the probability,  $P(x, y) dx dy$ , that the resultant structure amplitude  $F$  has components between  $x$  and  $x+dx$ ,  $y$  and  $y+dy$ , or alternatively the probability,  $P(I) dI$ , that the intensity,  $I \equiv FF^*$ , lies between  $I$  and  $I+dI$ . This problem is clearly very similar to that of the probability of Brownian motion producing a given displacement in a given time (Einstein, 1905), and analogy suggests that

$$P(x, y) dx dy = (\pi\Sigma)^{-1} \exp\{-(x^2 + y^2)/\Sigma\} dx dy, \quad (2)$$

where

$$\Sigma = \sum_{j=1}^N f_j^2. \quad (3)$$

Since  $I = x^2 + y^2$ , the probability that  $I$  will lie between  $I$  and  $I+dI$  is the same as the probability that  $(x, y)$  will lie in an annulus between radii  $\sqrt{I}$  and  $\sqrt{I+d(\sqrt{I})}$ , so that

$$\begin{aligned} P(I) dI &= 2\pi \cdot P(x, y) \cdot \sqrt{I} \cdot d(\sqrt{I}) \\ &= \Sigma^{-1} \exp\{-I/\Sigma\} dI. \end{aligned} \quad (4)$$

These expressions are, in fact, correct for crystals without symmetry elements. They may be verified in various ways, such as by considering the effect on  $F$  of introducing an  $(N+1)$ th atom into the cell, but the most satisfactory approach is probably via the so-called *central limit theorem*, particularly when the symmetry elements are to be taken into account.

The central limit theorem (Cramér, 1937, pp. 56-60) states that the sum of a sufficiently large number  $N$  of random variables  $\xi_j$  with mean values  $x_j$  and mean-square deviations  $\alpha_j^2$  is normally distributed about

$$X = \sum_{j=1}^N x_j, \quad (5)$$

with mean-square deviation

$$A^2 = \sum_{j=1}^N \alpha_j^2, \quad (6)$$

whatever the distribution functions of the individual random variables. In the present problem the real and imaginary parts of the contribution of each set of equivalent atoms may be regarded as random variables; the relations between the atoms of the set make it impossible to regard the contributions of each atom as random. The distribution functions for a crystal without symmetry elements will now be considered in some detail, and then the effect of certain elements will be considered briefly.

## 2. Distribution functions in particular cases

### 2.1. No symmetry

The contribution of each atom is in this case a random variable. For the real part of  $F$

$$\xi_j = f_j \cos(2\pi \mathbf{s} \cdot \mathbf{r}_j), \quad (7)$$

$$\text{where } \mathbf{s} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (8)$$

is the position vector in the reciprocal lattice, and

$$\mathbf{r}_j = u_j\mathbf{a} + v_j\mathbf{b} + w_j\mathbf{c} \quad (9)$$

is the position vector of the  $j$ th atom within the unit cell of the crystal. The variable  $\xi_j$  is periodic with periods  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$ ; for definiteness it is convenient to choose the origin of  $\mathbf{r}_j$  at the 'centre of gravity' of the cell, so that

$$\sum_{j=1}^N f_j \mathbf{r}_j = 0. \quad (10)$$

The greatest numerical values of  $u_j$ ,  $v_j$ ,  $w_j$  will then be of the order of one-half. For large  $s$  the cosine factor in (7) takes on both positive and negative values as the direction of  $\mathbf{s}$  changes, so that the mean value  $x_j$  of  $\xi_j$  (averaged over various directions of  $\mathbf{s}$ ) is approximately zero, and its mean-square deviation from its mean value is  $\alpha_j^2 = \frac{1}{2}f_j^2$ . The value of  $A^2$  is then

$$A^2 = \sum_{j=1}^N \alpha_j^2 = \frac{1}{2} \sum_{j=1}^N f_j^2 = \frac{1}{2}\Sigma, \quad (11)$$

and the probability that the real part of the structure amplitude lies between  $x$  and  $x+dx$  is

$$P(x) dx = (2\pi)^{-\frac{1}{2}} A^{-1} \exp\{-x^2/2A^2\} dx \\ = (\pi\Sigma)^{-\frac{1}{2}} \exp\{-x^2/\Sigma\} dx. \quad (12)$$

Similarly for the imaginary part

$$\left. \begin{aligned} \eta_j &= f_j \sin(2\pi \mathbf{s} \cdot \mathbf{r}_j), \\ y_j &= \langle \eta_j \rangle = 0, \\ \beta_j^2 &= \langle (\eta_j - y_j)^2 \rangle = \frac{1}{2}f_j^2, \\ B^2 &= \sum_{j=1}^N \beta_j^2 = \frac{1}{2} \sum_{j=1}^N f_j^2 = \frac{1}{2}\Sigma, \\ P(y) dy &= (\pi\Sigma)^{-\frac{1}{2}} \exp\{-y^2/\Sigma\} dy, \end{aligned} \right\} \quad (13)$$

where the angle brackets  $\langle \rangle$  denote mean values over various directions of  $\mathbf{s}$ . The probability that  $x$  will lie

between  $x$  and  $x+dx$ ,  $y$  between  $y$  and  $y+dy$ , is therefore

$$P(x, y) dx dy = P(x) P(y) dx dy \\ = (\pi\Sigma)^{-1} \exp\{-(x^2+y^2)/\Sigma\} dx dy, \quad (14)$$

in agreement with (2).

Equation (14) is, however, based on the assumptions that

$$x_j = f_j \langle \cos(2\pi \mathbf{s} \cdot \mathbf{r}_j) \rangle = 0, \quad (15)$$

$$y_j = f_j \langle \sin(2\pi \mathbf{s} \cdot \mathbf{r}_j) \rangle = 0, \quad (16)$$

$$\alpha_j^2 = \langle [x_j - f_j \cos(2\pi \mathbf{s} \cdot \mathbf{r}_j)]^2 \rangle = \frac{1}{2}f_j^2, \quad (17)$$

$$\beta_j^2 = \langle [y_j - f_j \sin(2\pi \mathbf{s} \cdot \mathbf{r}_j)]^2 \rangle = \frac{1}{2}f_j^2. \quad (18)$$

Equation (16) is, in fact, always valid, since for every reflexion  $hkl$  there is another  $\bar{h}\bar{k}\bar{l}$  with the opposite value of  $\eta_j$ , but the others are only limiting values for large  $s$ . For small  $s$  the distribution function will have the form

$$P(x, y) dx dy \\ = (2\pi AB)^{-1} \exp\{-(x-X)^2/2A^2 - y^2/2B^2\} dx dy, \quad (19)$$

where  $X$  is not necessarily zero and  $A$  and  $B$  are not equal. The mean value of the intensity will then be

$$\langle I \rangle = \iint (x^2 + y^2) P(x, y) dx dy \\ = (2\pi AB)^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (x^2 + y^2) \\ \times \exp\{-(x-X)^2/2A^2 - y^2/2B^2\} dx dy \\ = A^2 + B^2 + X^2. \quad (20)$$

2.1.1. The values of the functions averaged in equations (15)–(18) should be those for  $\mathbf{s}$  at the discrete points of the reciprocal lattice, but for large  $N$  the average over the discrete points will approximate to averages over regions of reciprocal space. There are two ways of averaging of particular importance: the general case where the average value for the general reflexions  $hkl$  is taken for all values of  $hkl$  giving approximately the same value of  $s$ , and the special case when the average value for a zone of reflexions (say  $hk0$ ) is taken for all values of  $h$  and  $k$  giving approximately the same values of  $s$ . In the general case, with polar co-ordinates  $s$ ,  $\psi$ ,  $\phi$  chosen with the axis parallel to  $\mathbf{r}_j$ , (15) becomes

$$x_j = (f_j/4\pi) \int_0^\pi \int_0^{2\pi} \cos(2\pi r_j s \cos \psi) \sin \psi d\psi d\phi \\ = f_j \frac{\sin(2\pi r_j s)}{2\pi r_j s}. \quad (21)$$

This approaches zero for  $s$  large, but  $f_j$  for  $s$  small. Equation (17) becomes

$$\alpha_j^2 = \langle \xi_j^2 \rangle - x_j^2 \\ = (f_j^2/4\pi) \int_0^\pi \int_0^{2\pi} \cos^2(2\pi r_j s \cos \psi) \sin \psi d\psi d\phi \\ - f_j^2 \frac{\sin^2(2\pi r_j s)}{(2\pi r_j s)^2} \\ = \frac{1}{2}f_j^2 \left[ 1 + \frac{\sin 4\pi r_j s}{4\pi r_j s} - \frac{2 \sin^2(2\pi r_j s)}{(2\pi r_j s)^2} \right], \quad (22)$$

which approaches  $\frac{1}{2}f_j^2$  for  $s$  large, but zero for  $s$  small. Similarly (18) becomes

$$\beta_j^2 = \frac{1}{2}f_j^2 \left[ 1 - \frac{\sin 4\pi r_j s}{4\pi r_j s} \right], \quad (23)$$

which is  $\frac{1}{2}f_j^2$  for  $s$  large, but zero for  $s$  small. In order to calculate  $X$ ,  $A$ ,  $B$  equations (21)–(23) have to be summed for all values of  $j$ . For small  $s$  they may be expanded in even powers of  $s$ , so that  $X$  depends on the zeroth, second, fourth, ... moments of the cell about its centre of gravity, and  $A$  and  $B$  depend on the zeroth, second, ... moments of a cell with atoms of weight  $f_j^2$  about its centre of gravity. These moments involve a knowledge of the crystal structure, but for  $N$  large they cannot be far from those of a cell with the same number of electrons distributed uniformly. With

$$H = \sum_{j=1}^N f_j, \quad (24)$$

$$m_k = U^{-1} \int_U r^k dU, \quad (25)$$

where  $U$  is the volume of one unit cell,

$$N_k = \sum_{j=1}^N f_j r_j^k \doteq H m_k, \quad (26)$$

$$M_k = \sum_{j=1}^N f_j^2 r_j^k \doteq \Sigma m_k, \quad (27)$$

the expressions for  $X$ ,  $A$ ,  $B$  become

$$X = \sum_{j=1}^N x_j = N_0 - \frac{2}{3}N_2(\pi s)^2 + \frac{2}{15}N_4(\pi s)^4 - \dots, \quad (28)$$

$$\doteq H \left[ 1 - \frac{2}{3}m_2(\pi s)^2 + \frac{2}{15}m_4(\pi s)^4 - \dots \right], \quad (29)$$

$$A^2 = \sum_{j=1}^N \alpha_j^2 = \frac{16}{45}M_4(\pi s)^4 - \frac{64}{315}M_6(\pi s)^6 + \dots, \quad (30)$$

$$\doteq \Sigma \left[ \frac{16}{45}m_4(\pi s)^4 - \frac{64}{315}m_6(\pi s)^6 + \dots \right], \quad (31)$$

$$B^2 = \sum_{j=1}^N \beta_j^2 = \frac{4}{3}M_2(\pi s)^2 - \frac{16}{15}M_4(\pi s)^4 + \dots, \quad (32)$$

$$\doteq \Sigma \left[ \frac{4}{3}m_2(\pi s)^2 - \frac{16}{15}m_4(\pi s)^4 + \dots \right], \quad (33)$$

$$\langle I \rangle = N_0^2 - \frac{4}{3}(N_0 N_2 - M_2)(\pi s)^2 + \frac{4}{3}(\frac{1}{3}N_0 N_4 + \frac{1}{3}N_2^2 - \frac{3}{15}M_4)(\pi s)^4 + \dots \quad (34)$$

For large  $s$  the values of  $X$ ,  $A^2$ ,  $B^2$  oscillate about the asymptotic values (equations (21)–(23))

$$X \sim 0, \quad (35)$$

$$A^2 \sim \frac{1}{2} \sum_{j=1}^N f_j^2 [1 - (2\pi r_j s)^{-2}] \\ = \frac{1}{2} \Sigma - M_{-2}/8\pi^2 s^2 \quad (36)$$

$$\doteq \frac{1}{2} \Sigma [1 - m_{-2}/4\pi^2 s^2], \quad (37)$$

$$B^2 \sim \frac{1}{2} \sum_{j=1}^N f_j^2 = \frac{1}{2} \Sigma. \quad (38)$$

It has not been found possible to obtain an asymptotic value for  $\langle I \rangle$ , other than  $\Sigma$ ; substitution of the values of  $A^2$ ,  $B^2$  and  $X^2$  in (20) gives

$$\langle I \rangle = \Sigma + \sum_{j \neq j'} f_j f_{j'} \frac{\sin(2\pi r_j s)}{2\pi r_j s} \frac{\sin(2\pi r_{j'} s)}{2\pi r_{j'} s}, \quad (39)$$

and the sum in this equation appears to have no simple

interpretation. The main interest in these calculations lies in the possibility of using  $\langle I \rangle$  to put relative intensities on an absolute basis. It is, therefore, important to make some estimate of the minimum value of  $s$  for which  $\langle I \rangle$  has practically reached its asymptotic value. This can be approached in two ways: from (34) and from (39). If  $f$  is an 'average' atomic scattering factor and  $a$  an 'average' cell dimension,  $N_0 \doteq Nf$ ,  $N_2 \doteq \frac{1}{4}Nfa^2$ ,  $M_2 \doteq \frac{1}{4}Nf^2a^2$ , so that

$$\langle I \rangle \doteq N^2 f^2 \{ 1 - \frac{1}{3}(1 - N^{-1})(\pi a s)^2 + \dots \}. \quad (40)$$

This falls to half value for  $s \doteq 0.4a^{-1}$ , so it is reasonable to suppose that for practical purposes it reaches its asymptotic value for  $s$  a small multiple of this, say  $2a^{-1}$ . Alternatively, the sum in (39) consists of  $N(N-1)$  terms of random sign and average magnitude less than  $[fm_{-1}(2\pi s)^{-1}]^2$ , so that

$$\langle I \rangle \sim \Sigma + O\{\sqrt{[N(N-1)][fm_{-1}(2\pi s)^{-1}]^2}\} \quad (41)$$

$$= \Sigma [1 + O\{(4as)^{-2}\}], \quad (42)$$

where  $O\{\}$  means 'of the order of magnitude of'. The smallest deviation from  $\Sigma$  worth considering is probably of the order of 10%, which means that  $s$  should be greater than  $a^{-1}$ , an estimate of the same order of magnitude as that obtained from (34). In using the mean value of  $I$  to put intensities on an absolute basis, therefore, the region of averaging should not include reflexions that have not at least one index of 2 or greater. In view of the approximate nature of the estimates involved, some care in using this criterion is necessary when the axes are of very different lengths.

2.1.2. In the special case of a zone of intensities (15) becomes, with the axis of polar co-ordinates  $s$ ,  $\psi$  perpendicular to  $\mathbf{r}_j$  and the zone axis,

$$x_j = \frac{f_j}{2\pi} \int_0^{2\pi} \cos(2\pi r_j' s \sin \psi) d\psi \\ = f_j J_0(2\pi r_j' s), \quad (43)$$

where  $J_0$  is the Bessel function of order zero and  $r_j'$  is the projection of  $\mathbf{r}_j$  on the plane perpendicular to the zone axis. Like (21), this approaches zero for  $s$  large,  $f_j$  for  $s$  small. Equations (17) and (18) become

$$\alpha_j^2 = \langle \xi_j^2 \rangle - x_j^2 \\ = \frac{1}{2}f_j^2 [1 + J_0(4\pi r_j' s) - 2J_0^2(\pi r_j' s)], \quad (44)$$

$$\text{and } \beta_j^2 = \langle \eta_j^2 \rangle = \frac{1}{2}f_j^2 [1 - J_0(4\pi r_j' s)], \quad (45)$$

approaching  $\frac{1}{2}f_j^2$  for  $s$  large, zero for  $s$  small. Power series expansions for small  $s$  give

$$x_j = f_j [1 - (\pi s)^2 r_j'^2 + \frac{1}{4}(\pi s)^4 r_j'^4 - \dots], \quad (46)$$

$$X = N_0 - N_2(\pi s)^2 + \frac{1}{4}N_4(\pi s)^4 - \dots, \quad (47)$$

$$\doteq H [1 - m_2(\pi s)^2 + \frac{1}{4}m_4(\pi s)^4 - \dots], \quad (48)$$

$$\alpha_j^2 = f_j^2 \left[ \frac{1}{2}(\pi s)^4 r_j'^4 - \frac{1}{3}(\pi s)^6 r_j'^6 + \dots \right], \quad (49)$$

$$A^2 = \frac{1}{2}M_4(\pi s)^4 - \frac{1}{3}m_6(\pi s)^6 + \dots, \quad (50)$$

$$\doteq \Sigma \left[ \frac{1}{2}m_4(\pi s)^4 - \frac{1}{3}m_6(\pi s)^6 + \dots \right], \quad (51)$$

$$\beta_j^2 = f_j^2 \left[ 2(\pi s)^2 r_j'^2 - 2(\pi s)^4 r_j'^4 + \dots \right], \quad (52)$$

$$B^2 = 2M_2(\pi s)^2 - 2M_4(\pi s)^4 + \dots, \quad (53)$$

$$\doteq \Sigma \left[ 2M_2(\pi s)^2 + 2m_4(\pi s)^4 + \dots \right], \quad (54)$$

$$\langle I \rangle = N_0^2 - 2(N_0 N_2 - M_2)(\pi s)^2 + \frac{1}{2}(N_0 N_4 + 2N_2^2 - 3M_4)(\pi s)^4 - \dots, \quad (55)$$

where the  $N$ 's,  $M$ 's and  $m$ 's are polar moments of inertia about the zone axis. For  $s$  large,  $X$ ,  $A^2$ ,  $B^2$  oscillate about the values  $X=0$ ,  $B^2=\frac{1}{2}\Sigma$ , and

$$A^2 = \frac{1}{2}\Sigma - \frac{1}{2\pi} M_{-1}(\pi s)^{-1} + \dots \quad (56)$$

$$\div \frac{1}{2}\Sigma [1 - m_{-1}(2\pi^2 s)^{-1} + \dots]. \quad (57)$$

The asymptotic value of  $\langle I \rangle$  is again  $\Sigma$ . An estimate of the minimum value of  $s$  for which it is safe to assume that  $\langle I \rangle$  has this value, by the same methods as in § 2.1.1, gives the same result,  $s > 2a^{-1}$ .

### 2.2. Centre of symmetry

The atoms are in pairs related by a centre of symmetry, so that

$$\xi_j = 2f_j \cos(2\pi s \cdot \mathbf{r}_j), \quad (58)$$

$$\eta_j \equiv 0, \quad (59)$$

and for large  $s$

$$x_j = \langle \xi_j \rangle = 0, \quad y_j \equiv 0, \quad (60)$$

$$X = \sum_{j=1}^{\frac{1}{2}N} x_j = 0, \quad (61)$$

$$A^2 = \sum_{j=1}^{\frac{1}{2}N} \alpha_j^2 = 2 \sum_{j=1}^{\frac{1}{2}N} f_j^2 = \Sigma, \quad (62)$$

$$P(x) dx = (2\pi)^{-\frac{1}{2}} A \exp\{-x^2/2A^2\}, \\ = (2\pi\Sigma)^{-\frac{1}{2}} \exp\{-x^2/2\Sigma\} dx, \quad (63)$$

$$P(y) dy = \delta(y, 0) dy, \quad (64)$$

where  $\delta(y, 0)$  is the delta function ( $\delta(y, 0) = 0$ ,  $y \neq 0$ ,  $\int_{-\infty}^{\infty} \delta(y, 0) dy = 1$ ). Equation (63) expresses Hughes's empirical result.

### 2.3. Centring

A centred crystal can always be referred to a primitive lattice, and if this is done the preceding discussion applies without change. If, however, the centred lattice is retained, many reflexions have intensities identically zero, and the average value of the non-zero intensities is increased, so that the average of all intensities, zero and non-zero, remains at  $\Sigma$ . The distribution function can be written formally

$$P(I) = (k-1)k^{-1} \delta(I, 0) + (k^2\Sigma)^{-1} \exp\{-I/k\Sigma\}, \quad (65)$$

where  $k$  is 4 for a face-centred crystal and 2 for an end- or body-centred crystal. If the crystal is centrosymmetric as well as centred,

$$P(x) = (k-1)k^{-1} \delta(x, 0) + (2\pi k^3\Sigma)^{-\frac{1}{2}} \exp\{-x^2/2k\Sigma\}. \quad (66)$$

### 2.4. Other symmetry elements

Other symmetry elements do not affect enough intensities to change the distribution function for the  $hkl$  intensities, but may effect zones. For example, the  $h0l$  zone for crystals with a diad axis behaves as if centro-

symmetric, crystals with a glide plane have a zone that behaves as if centred, and crystals with a screw axis have a line of intensities that behave as if centred.

A word of warning is perhaps desirable. The whole analysis rests on there being a sufficient number of atoms 'randomly' distributed. When this condition is not fulfilled, for example when the structure is dominated by a heavy atom, or when there is a superstructure or other pseudosymmetry in atomic arrangement, the intensity-distribution function is abnormal. It is likely that individual treatment of such cases would yield useful results, but it does not seem worth while at the present stage to attempt a general treatment.

### 3. Possible detection of centres of symmetry

The preceding discussion may perhaps put the  $\langle I \rangle$  method of determining absolute from relative intensities on a firmer basis. It opens up, however, the possibility of a purely X-ray determination of the presence or absence of a centre of symmetry, since the distribution function takes different forms in these cases. The best practical approach would probably be through a comparison of  $\langle |F| \rangle$  and  $\langle I \rangle$ ; for non-centrosymmetric crystals

$$\langle |F| \rangle = \Sigma^{-1} \int_0^{\infty} \sqrt{I} \exp\{-I/\Sigma\} dI \\ = \frac{1}{2}(\pi\Sigma)^{\frac{1}{2}}, \quad (67)$$

and for centrosymmetric crystals

$$\langle |F| \rangle = (2\pi\Sigma)^{-\frac{1}{2}} \int_0^{\infty} \exp\{-I/2\Sigma\} dI \\ = (2\Sigma/\pi)^{\frac{1}{2}}. \quad (68)$$

$$\text{Thus } \rho \equiv \langle |F| \rangle^2 / \langle I \rangle = \pi/4 \div 0.785 \quad (69)$$

in non-centrosymmetric crystals, and

$$\rho = 2/\pi \div 0.637 \quad (70)$$

in centrosymmetric crystals. The difference between the ratios 0.785 and 0.637 is not great, but may suffice with accurate intensity measurements. (The measurements need not be put on an absolute scale in making this comparison. For centred crystals the ratios are divided by  $k$ .) There is a larger percentage difference between the two values of  $\langle I^2 \rangle$ , but experimental errors are multiplied and there may be no real advantage.

### References

- CRAMÉR, H. (1937). *Random Variables and Probability Distributions*. Cambridge: University Press.  
 EINSTEIN, A. (1905). *Ann. Phys., Lpz.* (IV), **17**, 549.  
 HARKER, D. (1948). *Amer. Min.* **33**, 764.  
 HETTICH, A. (1935). *Z. Kristallogr.* **91**, 154.  
 HUGHES, E. W. (1949). *Acta Cryst.* **2**, 34.  
 WILSON, A. J. C. (1942). *Nature, Lond.*, **150**, 152.