$$
\begin{aligned}
\theta(Z_{\mathbf{h},\mathbf{h}'})dZ_{\mathbf{h},\mathbf{h}'}
&= 2\int_{y=0}^{\infty}\frac{1}{y}P(y)\mu\left(\frac{Z_{\mathbf{h},\mathbf{h}'}}{y}\right)dy\,dZ_{\mathbf{h},\mathbf{h}'}\\
&= (\pi\varepsilon_2)^{-1}\int_{y=0}^{\infty}\frac{1}{y}\exp\left(-\frac{y^2}{2\varepsilon_2}\right)\\
&\qquad\times\exp\left[-\frac{(Z_{\mathbf{h},\mathbf{h}'}/y-V_{\mathbf{h}}y/\varepsilon_2)^2}{2\varepsilon_2}\right]dy\,dZ_{\mathbf{h},\mathbf{h}'}\\
&= (\pi\varepsilon_2)^{-1}\exp\left(\frac{Z_{\mathbf{h},\mathbf{h}'}V_{\mathbf{h}}}{\varepsilon_2^2}\right)\\
&\quad\times\int_{y=0}^{\infty}\frac{1}{y}\exp\left[-\frac{1}{2\varepsilon_2}\left\{y^2\left(1+\frac{V_{\mathbf{h}}^2}{\varepsilon_2^2}\right)+\frac{Z_{\mathbf{h},\mathbf{h}'}^2}{y^2}\right\}\right]dy\,dZ_{\mathbf{h},\mathbf{h}'}\\
&= (\pi\varepsilon_2)^{-1}\exp\left(\frac{Z_{\mathbf{h},\mathbf{h}'}V_{\mathbf{h}}}{\varepsilon_2^2}\right)K_0\left[\frac{Z_{\mathbf{h},\mathbf{h}'}}{\varepsilon_2}\left(1+\frac{V_{\mathbf{h}}^2}{\varepsilon_2^2}\right)^{\frac{1}{2}}\right]dZ_{\mathbf{h},\mathbf{h}'}\,,
\end{aligned}
$$

where $K_0(x)$ is a zero-order Bessel function of the third kind (Watson, 1922, p. 123).

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Some Observations on the Probability Distribution of X-ray Intensities

By A. Hargreaves

Physics Department, College of Technology, Manchester 1, *England*

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Wilson's theory for the probability distribution of X-ray intensities applies only when the unit cell contains a number of atoms of similar scattering power. Consideration is given to the way the distribution is modified when the intensities are dominated by a single atom in the unit of pattern of the structure.

1. Introduction

A theoretical investigation of the probability distribution of reflected X-ray intensities (Wilson, 1949) has been developed (Howells, Phillips & Rogers, 1950) to give a simple method of distinguishing between centrosymmetrical and non-centrosymmetrical structures. If each intensity is expressed as a fraction, z, of the local average intensity, then the fractions, $N(z)$, of the reflexions whose intensities are less than or equal to z are

$$_1N(z) = 1-\exp(-z)$$

for a non-centrosymmetrical structure

and

$$_{\bar{1}}N(z) = \operatorname{erf}(\tfrac{1}{2}z)^{\frac{1}{2}}$$

for a centrosymmetrical structure.

The functions $_1N(z)$ and $_{\bar{1}}N(z)$ are plotted in Fig. 1.

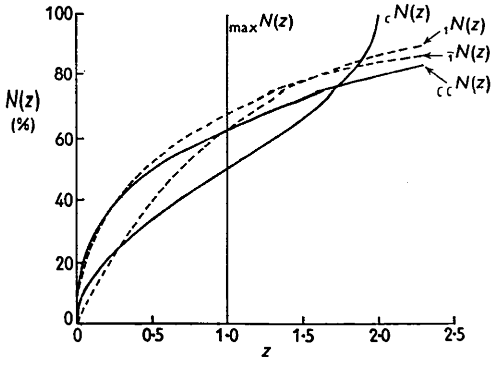

Fig. 1. Comparison of the functions $_1N(z)$, $_{\bar{1}}N(z)$, $_{\max.}N(z)$, $_cN(z)$ and $_{cc}N(z)$.

Wilson has pointed out that his analysis depends on there being a sufficient number of atoms 'randomly' distributed in the unit cell. This condition is not satisfied in two cases of practical importance (i) when certain types of pseudosymmetry originate from the atomic arrangement, (ii) when the intensity distribution is dominated by a small number of heavier atoms. $N(z)$ functions applicable to case (i) have been derived by Lipson & Woolfson (1952) and by Rogers & Wilson (1953). Functions appropriate in case (ii) will vary with each structure, but some idea of their nature may be obtained by considering the extreme case in which one heavy atom, in a general position in the unit of pattern of the structure, completely dominates the remaining lighter atoms.

2. Distribution of intensities for one atom in a general position

The intensity distribution is dependent upon the space-group symmetry and may be used as an aid in the determination of space groups; zones of reflexions help to distinguish between the 17 plane groups and their distributions are of particular importance. Discussion will be limited to a consideration of the 9 plane groups representing projections of the triclinic, monoclinic and orthorhombic systems.

The real and imaginary parts of the geometrical structure factors can be combined when only one atom in each general position is considered to be effective in scattering X-rays; the resulting expressions are given in Table 1.

The geometrical structure factors in Table 1 are of three types only; corresponding to them there are three different distributions of the X-ray intensities.

(i) *Plane group p*1

For this plane group the geometrical structure factor is unity. Each intensity has the maximum possible value and is equal to the local average intensity. The distribution function is represented in Fig. 1 by a vertical line ${}_{\max.}N(z)$ passing through $z = 1{\cdot}0$.

(ii) *Plane groups p2, pm, pg, cm*

All geometrical structure factors are of the form $\cos X$. If the maximum intensity is taken to be unity, then the average intensity is the average value of $\cos^2 X$, which is 0·5. Possible values of z therefore lie between the limits 0·0 and 2·0. The function $N(z)$ represents the fraction of a period, $(2\pi - X)/2\pi$, for which the intensities are equal to or less than $\cos^2 X$; it is plotted as ${}_{c}N(z)$ in Fig. 1.

(iii) *Plane groups pmm, pmg, pgg, cmm*

All geometrical structure factors are of the form $\cos X . \cos Y$. The average intensity is 0·25, the average value of $(\cos X . \cos Y)^2$, so that the range of z is 0·0 to 4·0. The $N(z)$ function represents the distribution of the values of $(\cos X . \cos Y)^2$ when X and Y are varied at random. Constant values of $(\cos X . \cos Y)^2$ are represented by the contour lines of constant $(\cos X . \cos Y)$ in one of the well known Bragg–Lipson charts (see, for example, Lipson & Cochran, 1953). The distribution of the values of $(\cos X . \cos Y)^2$ is therefore given by the relative areas of the chart below each contour line. These areas can be deduced with sufficient accuracy by using a planimeter. Alternatively, they can be derived to any desired degree of accuracy by evaluating an integral related to a complete elliptic integral of the first kind (Bowman, 1953). I am indebted to Dr L. R. Shenton, of the College Mathematics Department, for this solution, which leads to the distribution

$$
\begin{aligned}
{}_{cc}N(z) = \frac{4}{\pi^2}\Bigg\{ & \frac{\sqrt{z}}{2}\left(\log_e \frac{8}{\sqrt{z}} + 1\right) \\
& + \left(\frac{1}{3}\right)\left(\frac{1}{2}\right)^2\left(\frac{\sqrt{z}}{2}\right)^3\left(\log_e \frac{8}{\sqrt{z}} + \frac{1}{3} - \frac{2}{1\times 2}\right) \\
& + \left(\frac{1}{5}\right)\left(\frac{1\times 3}{2\times 4}\right)^2\left(\frac{\sqrt{z}}{2}\right)^5\left(\log_e \frac{8}{\sqrt{z}} + \frac{1}{5} - \frac{2}{1\times 2} - \frac{2}{3\times 4}\right) \\
& + \left(\frac{1}{7}\right)\left(\frac{1\times 3\times 5}{2\times 4\times 6}\right)^2\left(\frac{\sqrt{z}}{2}\right)^7 \\
& \times \left(\log_e \frac{8}{\sqrt{z}} + \frac{1}{7} - \frac{2}{1\times 2} - \frac{2}{3\times 4} - \frac{2}{5\times 6}\right) + \ldots \Bigg\} .
\end{aligned}
$$

The ${}_{cc}N(z)$ distribution is plotted in Fig. 1.

Table 1. *Geometrical structure factors for an atom in the oblique and rectangular plane groups*

Plane group	Lattice type	Presence or absence of symmetry centres	Geometrical structure factor
*p*1	Oblique	1	1 (unity)
*p*2	Oblique	$\bar{1}$	$2 \cos 2\pi(hx+ky)$
pm	Rectangular	1	$2 \cos 2\pi hx$
pg	Rectangular	1	$2 \cos 2\pi hx$ when $k = 2n$ $-2 \sin 2\pi hx$ when $k = 2n+1$
cm	Rectangular	1	$4 \cos 2\pi hx$
pmm	Rectangular	$\bar{1}$	$4 \cos 2\pi hx . \cos 2\pi ky$
pmg	Rectangular	$\bar{1}$	$4 \cos 2\pi hx . \cos 2\pi ky$ when $h = 2n$ $-4 \sin 2\pi hx . \sin 2\pi ky$ when $h = 2n+1$
pgg	Rectangular	$\bar{1}$	$4 \cos 2\pi hx . \cos 2\pi ky$ when $h+k = 2n$ $-4 \sin 2\pi hx . \sin 2\pi ky$ when $h+k = 2n+1$
cmm	Rectangular	$\bar{1}$	$8 \cos 2\pi hx . \cos 2\pi ky$

3. Examples

(i) 9-para-*Carbethoxyphenyl*-9-*stibiafluorene*

Space group $P\bar{1}$; 2 molecules of $C_{20}H_{17}O_2.Sb$ per unit cell.

The $N(z)$ distribution of the $0kl$ reflexions is shown in Fig. 2. It can be seen that the distribution approximates far more closely to that appropriate to a heavy atom in the plane group $p2$, viz. ${}_cN(z)$, than to the centrosymmetric distribution ${}_{\bar{1}}N(z)$ which would be expected for a number of atoms of similar weight; this is due to the dominating effect of the antimony atom (atomic number 51).

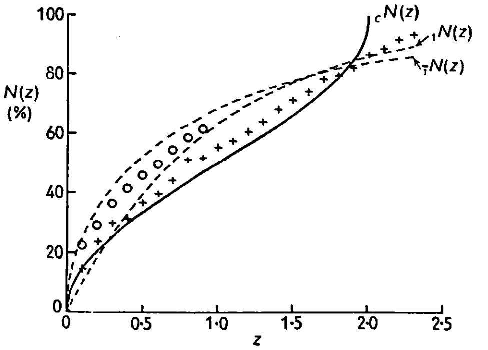

Fig. 2. Comparison of the experimental distributions $N(z)$ for 9-*para*-carbethoxyphenyl-9-stibiafluorene (marked by crosses) and for *l*-ephedrine hydrobromide (marked by circles) with the theoretical distributions ${}_1N(z)$, ${}_{\bar{1}}N(z)$ and ${}_cN(z)$.

(ii) l-*Ephedrine hydrobromide*

Space group $P2_1$; 2 molecules of $C_{10}H_{15}ON.HBr$ per unit cell.

The experimental $N(z)$ distribution for the centrosymmetrical [010] projection has been published by Howells, Phillips & Rogers (1950) and is reproduced in Fig. 2. This example is analogous to the previous one but the bromine atom (atomic number 35) in *l*-ephedrine hydrobromide is less dominating than the antimony atom in 9-*para*-carbethoxyphenyl-9-stibiafluorene. The experimental distribution now lies nearer to the ${}_{\bar{1}}N(z)$ curve than to the ${}_cN(z)$ curve.

(iii) *Longifolene hydrobromide*

Space group $P2_12_12_1$; 4 molecules of $C_{15}H_{25}Br$ per unit cell.

The experimental $N(z)$ curve for the $0kl$ reflexions may be expected to lie between the functions ${}_{\bar{1}}N(z)$ and ${}_{cc}N(z)$: ${}_{\bar{1}}N(z)$ would be the appropriate distribution for the centrosymmetrical [100] projection if all atoms had equal weight, whilst ${}_{cc}N(z)$ would be the distribution function, applicable to the plane group pgg, if the bromine atom completely outweighed the other atoms. The experimental $N(z)$ function may be compared with ${}_{\bar{1}}N(z)$ and ${}_{cc}N(z)$ in Fig. 3.

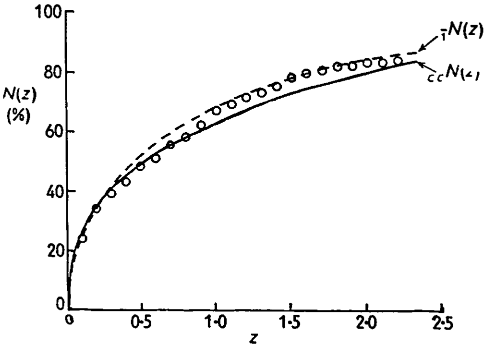

Fig. 3. Comparison of the experimental distribution $N(z)$ for longifolene hydrobromide (marked by circles) with the theoretical distributions ${}_{\bar{1}}N(z)$ and ${}_{cc}N(z)$.

4. Discussion

The examples described in § 3 all give experimental $N(z)$ functions which lie between the theoretical function, ${}_1N(z)$ or ${}_{\bar{1}}N(z)$, which holds when atoms of equal weight are arranged at random, and the function ${}_cN(z)$ or ${}_{cc}N(z)$, which is applicable when the heavy atom dominates the rest. Fig. 2 indicates that the experimental curve for *l*-ephedrine hydrobromide lies approximately midway between the curves ${}_1N(z)$ and ${}_{\bar{1}}N(z)$, and that the curve for 9-*para*-carbethoxyphenyl-9-stibiafluorene lies much nearer to ${}_1N(z)$ than to ${}_{\bar{1}}N(z)$ in spite of the fact that both structures are centrosymmetrical. It is evident that attempts to deduce the presence or absence of centrosymmetry from $N(z)$ curves must be approached with caution when heavy atoms are present; this conclusion was predicted by Wilson (1949).

I wish to thank Mr R. H. Moffett for permission to use unpublished data on longifolene hydrobromide, and Mr B. Chaudhuri for supplying data on 9-*para*-carbethoxyphenyl-9-stibiafluorene. Dr L. R. Shenton's assistance is acknowledged in § 2.

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