

In order to show that the moments of A do not depend on a linear relationship between h and k let us assume that $N_1h = N_2k$, where N_1 and N_2 are integers, and therefore we can put $h = N_2\lambda$, $k = N_1\lambda$, where λ varies in such a way that h and k assume integer values. If we now interpret $2\pi\lambda x$ and $2\pi\lambda y$ as independent random variables, θ and φ respectively, equation (A17) becomes

$$A = \cos \alpha + \cos \beta + \cos (\alpha + \beta),$$

where

$$\alpha = N_2\theta + N_1\varphi, \quad \beta = N_1\theta - (N_1 + N_2)\varphi.$$

The r th moment of A is now

$$\langle A^r \rangle = \iint A^r(\alpha, \beta) \left| \frac{\partial(\theta, \varphi)}{\partial(\alpha, \beta)} \right| d\alpha d\beta / 4\pi^2,$$

where the Jacobian is $(N_1^2 + N_1N_2 + N_2^2)^{-1}$ and the integration is taken over the parallelogram P with vertices at $(0, 0)$, $(2\pi N_1, 2\pi N_2)$, $(-2\pi N_2, 2\pi(N_1 + N_2))$ and $(-2\pi(N_1 + N_2), 2\pi N_1)$. Let I be

$$\int_0^{2\pi} \int_0^{2\pi} A^r(\alpha, \beta) d\alpha d\beta;$$

on enclosing P in a rectangle R with sides of length $2\pi(N_1 + N_2)$, $2\pi(2N_1 + N_2)$ parallel to the axes α and β , the integral of A^r over R is $(N_1 + N_2)(N_2 + 2N_1)I$. Now from the periodicity of the function A and from the fact that the vertices of P and R have coordinates which are multiples of 2π , the integral of A^r over the areas which are not common to P and R is equal to $(N_1^2 + 2N_1N_2)I$: therefore, the integral of A^r over P is $(N_1^2 + N_1N_2 + N_2^2)I$ from which

$$\begin{aligned} (N_1^2 + N_1N_2 + N_2^2)^{-1} \iint_P A^r(\alpha, \beta) d\alpha d\beta \\ = \int_0^{2\pi} \int_0^{2\pi} A^r(\alpha, \beta) d\alpha d\beta. \end{aligned}$$

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The Use of Moments of X-ray Intensity in Space-Group Determination. II. Practical Application

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Simple expressions for evaluating theoretical moments of the intensities of X-ray reflexions are tabulated. They cover crystals with any triclinic, monoclinic or orthorhombic space group and they are valid when the unit cell contains a small number of atoms and atoms of widely differing weights; consideration is given to the modifications required when atoms are present in special positions. The evaluation and comparison of theoretical and experimental moments are described and illustrated by examples which could not have been studied by the usual statistical tests.

1. Introduction

The r th moment of the intensity of a group of X-ray reflexions, $\langle I^r \rangle$, is defined as the average value of I^r ,

The variables $N_2\theta + N_1\varphi$ and $N_1\theta - (N_1 + N_2)\varphi$ can therefore be replaced by α and β , which are uniformly distributed in the range $(0-2\pi)$, and the moments of A^{2r} are independent of N_1 and N_2 giving $A = \cos \alpha + \cos \beta + \cos (\alpha + \beta)$ as the effective geometrical structure factor for statistical purposes. If we now put $\theta = (\alpha + \beta)/2$ and $\varphi = (\alpha - \beta)/2$ a similar analysis to the above leads to $A = \cos 2\theta + 2 \cos \theta \cos \varphi$ as another form for the purposes of statistical analysis.

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where values of I represent the intensities of the individual reflexions.

The methods described in Part I (Foster & Hargreaves, 1963), for deriving theoretical moments of

the intensities of X-ray reflexions, have been used to obtain the expressions for theoretical moments of intensity now presented in § 2 of Part II. These expressions involve summations extending over the atoms in the asymmetric unit of the cell and are valid even when the number of atoms in the unit cell is small or when some atoms differ considerably from others in weight. A comparison of theoretical and experimental moments of intensity provides, therefore, a test for crystal symmetry which can be applied to material of any composition. In contrast, most statistical tests for symmetry (*International Tables for X-ray Crystallography*, 1959) are valid only when the unit cell contains a large number of atoms of equal weight.

In this paper an account is given of the procedure for applying moment tests to determine the symmetry of crystals in the triclinic, monoclinic and orthorhombic systems. All the relevant theoretical expressions are presented in § 2; in using them it is unnecessary to refer to — or to understand — the underlying theory developed in Part I.

2. Theoretical moments

Moments of intensity depend, in a complicated way, on the types and relative positions of symmetry elements in the structure. A safe way of allowing for

interactions between the different symmetry elements is to calculate moments of intensity for the individual space groups, using intensities derived from the structure-factor formulae given in *International Tables for X-ray Crystallography* (1952). The intensities are obtained from

$$I(hkl) = \left(\sum_r f_r A_r\right)^2 + \left(\sum_r f_r B_r\right)^2,$$

where A and B are trigonometrical expressions which are listed in the *International Tables for X-ray Crystallography* for each space group and plane group, f_r is the scattering factor for the r th atom and the summations are taken over all the atoms in the asymmetric unit within the unit cell. Expressions giving moments of intensity may then be derived, using the methods described in Part I, for all but two of the 74 space groups and the 9 related plane groups in the triclinic, monoclinic and orthorhombic systems; the exceptions are $Fddd$ and $Fdd2$ which are, in any case, uniquely determinable from systematically absent reflexions. The first three moments of intensity for these space groups and plane groups are given in Table 1. Many of the expressions for moments of intensity are identical for two or more space groups and plane groups (apart from a numerical constant, which can be ignored for our purpose) because they are derived from similar structure-

Table 1. *Formulae used in calculating theoretical moments: all atoms in general positions*

	Geometrical structure factor		Moment of intensity
1.	$A = \cos \theta$	$B = \sin \theta$	$\langle I \rangle = S(2)$
	$A = \sin \theta$	$B = \cos \theta$	$\langle I^2 \rangle = 2S^2(2) - S(4)$
			$\langle I^3 \rangle = 6S^3(2) - 9S(2)S(4) + 4S(6)$
2.	$A = \cos \theta$	$B = 0$	$\langle I \rangle = \frac{1}{2}S(2)$
	$A = \sin \theta$	$B = 0$	$\langle I^2 \rangle = \frac{3}{4}S^2(2) - \frac{3}{8}S(4)$
			$\langle I^3 \rangle = \frac{15}{8}S^3(2) - \frac{45}{16}S(2)S(4) + \frac{5}{4}S(6)$
3.	$A = \cos \theta \cos \varphi$	$B = \cos \theta \sin \varphi$	$\langle I \rangle = \frac{1}{2}S(2)$
	$A = \cos \theta \sin \varphi$	$B = \cos \theta \cos \varphi$	$\langle I^2 \rangle = \frac{1}{2}S^2(2) - \frac{1}{8}S(4)$
	$A = \cos \theta \sin \varphi$	$B = \sin \theta \sin \varphi$	$\langle I^3 \rangle = \frac{3}{4}S^3(2) - \frac{9}{16}S(2)S(4) + \frac{1}{8}S(6)$
	$A = \sin \theta \sin \varphi$	$B = \sin \theta \cos \varphi$	
4.	$A = \cos \theta \cos \varphi$	$B = 0$	$\langle I \rangle = \frac{1}{4}S(2)$
	$A = \cos \theta \sin \varphi$	$B = 0$	$\langle I^2 \rangle = \frac{9}{16}S^2(2) - \frac{3}{64}S(4)$
	$A = \sin \theta \sin \varphi$	$B = 0$	$\langle I^3 \rangle = \frac{15}{64}S^3(2) - \frac{45}{256}S(2)S(4) + \frac{5}{128}S(6)$
5.	$A = \cos \theta \cos \varphi \cos \psi$	$B = \sin \theta \sin \varphi \sin \psi$	$\langle I \rangle = \frac{1}{4}S(2)$
	$A = \cos \theta \sin \varphi \sin \psi$	$B = \sin \theta \cos \varphi \cos \psi$	$\langle I^2 \rangle = \frac{1}{8}S^2(2) - \frac{1}{64}S(4)$
			$\langle I^3 \rangle = \frac{3}{32}S^3(2) - \frac{9}{256}S(2)S(4) + \frac{1}{256}S(6)$
6.	$A = \cos \theta \cos \varphi \cos \psi$	$B = \cos \theta \cos \varphi \sin \psi$	$\langle I \rangle = \frac{1}{4}S(2)$
	$A = \cos \theta \sin \varphi \sin \psi$	$B = \cos \theta \sin \varphi \cos \psi$	$\langle I^2 \rangle = \frac{1}{8}S^2(2) + \frac{1}{64}S(4)$
	$A = \cos \theta \sin \varphi \sin \psi$	$B = \sin \theta \sin \varphi \sin \psi$	$\langle I^3 \rangle = \frac{9}{32}S^3(2) + \frac{9}{256}S(2)S(4) - \frac{1}{32}S(6)$
7.	$A = \cos \theta \cos \varphi \cos \psi$	$B = 0$	$\langle I \rangle = \frac{1}{8}S(2)$
	$A = \cos \theta \cos \varphi \sin \psi$	$B = 0$	$\langle I^2 \rangle = \frac{3}{64}S^2(2) + \frac{3}{512}S(4)$
	$A = \cos \theta \sin \varphi \sin \psi$	$B = 0$	$\langle I^3 \rangle = \frac{15}{512}S^3(2) + \frac{45}{4096}S(2)S(4) - \frac{5}{512}S(6)$
	$A = 0$	$B = \sin \theta \sin \varphi \sin \psi$	
	$A = 0$	$B = \sin \theta \sin \varphi \cos \psi$	
	$A = 0$	$B = \sin \theta \cos \varphi \cos \psi$	

θ , φ and ψ each represent either $2\pi h_x$, $2\pi k_y$ or $2\pi l_z$, $\langle I^r \rangle$ is the r th moment of intensity, and $S(t) = \sum_1^n f_i^t$, where f_i is the scattering factor of the i th atom and the summation is taken over the n atoms in the asymmetric unit of the cell.

factor formulae; it will be seen that, for the 81 space groups and plane groups considered here, each moment is given by one of only 7 different expressions.

In using Table 1 to evaluate theoretical moments the first step is to obtain the appropriate values of A and B for the space groups and plane groups under consideration; these are given in the *International Tables for X-ray Crystallography* (1952). Neglecting the integer preceding the trigonometrical factor, the same values of A and B are then found in the left-hand column of Table 1; the corresponding expressions for moments of intensity are given alongside, in the right-hand column. Any convenient table of atomic scattering factors may be used in evaluating the summations $S(t)$; very accurate values are not required and temperature corrections are unnecessary. Finally, the moments of intensity are used to calculate the second and third moments of z , where z is defined as the ratio of the intensity of an X-ray reflexion to the local average intensity (Howells, Phillips & Rogers, 1950) and the r th moment of z is given by $\langle z^r \rangle = \langle I^r \rangle / \langle I \rangle^r$.

There are several reasons why it is preferable to compare theoretical and experimental moments of z rather than moments of intensity. Moments of z change much more slowly with Bragg angle and their use avoids the difficulty of obtaining the absolute scale and temperature factors which are required for comparing moments of intensity. Also, theoretical moments of z can be evaluated from summations $S(t)$ which extend over only the atoms in the asymmetric unit of the cell. Strictly, in Table 1, A , B and the moments of intensity should be multiplied by constants related to the number of equivalent positions in the unit cell. These constants can be neglected, however, when all atoms occupy general positions in the unit cell since they are eliminated in the evaluation of moments of z ; their omission greatly simplifies Table 1.

Atoms in special positions

When some of the atoms are in special positions in the unit cell it is necessary to consider the different multiplicities of equivalent positions for atoms in general and special positions; the constants related to these multiplicities, which appear in the *true* expressions for moments of intensity, are no longer eliminated in evaluating moments of z . The change in the geometrical structure-factor formula — to one containing fewer variables for the atoms in special positions — must also be taken into account.

Consider first the case when the contributions to the structure factors of atoms in special positions are given by A and B terms with the same number of the variables θ , φ and ψ — *i.e.* 2, 1 or 0 — for all such atoms. Quantities $\langle I_g^r \rangle$ and $\langle I_s^r \rangle$ may be evaluated by means of the formulae in Table 1 but with the summations $S(t)$ extending, respectively, over the atoms in general positions only and over the atoms

in special positions only. It may be shown, by the methods described in Part I, that the first three moments of intensity can then be calculated from the expressions given in Table 2. Moments of z are calculated from the moments of intensity in the usual way.

Table 2. *Formulae used in calculating theoretical moments: atoms in general and in special positions*

$$\begin{aligned}\langle I \rangle &= \langle I_g \rangle + \lambda^2 \langle I_s \rangle \\ \langle I^2 \rangle &= \langle I_g^2 \rangle + \lambda^4 \langle I_s^2 \rangle + K_1 \lambda^2 \langle I_g \rangle \langle I_s \rangle \\ \langle I^3 \rangle &= \langle I_g^3 \rangle + \lambda^6 \langle I_s^3 \rangle + K_2 \lambda^4 \langle I_g \rangle \langle I_s^2 \rangle + K_2 \lambda^2 \langle I_g^2 \rangle \langle I_s \rangle.\end{aligned}$$

λ is the ratio

$$\frac{\text{number of equivalent special positions in the unit cell}}{\text{number of equivalent general positions in the unit cell}}.$$

The value of K_1 is 6 for centrosymmetrical and 4 for non-centrosymmetrical plane groups and space groups, and the value of K_2 is 15 for centrosymmetrical and 9 for non-centrosymmetrical plane groups and space groups.

Each atom in a special position is counted as one complete atom in the summations $S(r)$ used to evaluate $\langle I_s^r \rangle$, even though atoms in special positions contribute only a fraction of their scattering power to the asymmetric unit; the constants λ introduce the appropriate corrections for the fractional contributions from atoms in special positions.

Table 3. *Formulae used in calculating theoretical moments: atoms in general and in different types of special position*

$$\begin{aligned}\langle I \rangle &= \langle I_g \rangle + \lambda_1^2 \langle I_1 \rangle + \lambda_2^2 \langle I_2 \rangle + \lambda_3^2 \langle I_3 \rangle \\ \langle I^2 \rangle &= \langle I_g^2 \rangle + \lambda_1^4 \langle I_1^2 \rangle + \lambda_2^4 \langle I_2^2 \rangle + \lambda_3^4 \langle I_3^2 \rangle \\ &\quad + K_1 \langle I_g \rangle \{ \lambda_1^2 \langle I_1 \rangle + \lambda_2^2 \langle I_2 \rangle + \lambda_3^2 \langle I_3 \rangle \} \\ &\quad + K_1 \{ \lambda_1^2 \lambda_2^2 \langle I_1 \rangle \langle I_2 \rangle + \lambda_1^2 \lambda_3^2 \langle I_1 \rangle \langle I_3 \rangle + \lambda_2^2 \lambda_3^2 \langle I_2 \rangle \langle I_3 \rangle \} \\ \langle I^3 \rangle &= \langle I_g^3 \rangle + \lambda_1^6 \langle I_1^3 \rangle + \lambda_2^6 \langle I_2^3 \rangle + \lambda_3^6 \langle I_3^3 \rangle \\ &\quad + K_2 \langle I_g^2 \rangle \{ \lambda_1^2 \langle I_1 \rangle + \lambda_2^2 \langle I_2 \rangle + \lambda_3^2 \langle I_3 \rangle \} \\ &\quad + K_2 \langle I_g \rangle \{ \lambda_1^4 \langle I_1^2 \rangle + \lambda_2^4 \langle I_2^2 \rangle + \lambda_3^4 \langle I_3^2 \rangle \} \\ &\quad + K_2 \{ \lambda_1^4 \lambda_2^2 \langle I_1^2 \rangle \langle I_2 \rangle + \lambda_1^4 \lambda_3^2 \langle I_1^2 \rangle \langle I_3 \rangle \\ &\quad + \lambda_2^4 \lambda_1^2 \langle I_2^2 \rangle \langle I_1 \rangle + \lambda_2^4 \lambda_3^2 \langle I_2^2 \rangle \langle I_3 \rangle \\ &\quad + \lambda_3^4 \lambda_1^2 \langle I_3^2 \rangle \langle I_1 \rangle + \lambda_3^4 \lambda_2^2 \langle I_3^2 \rangle \langle I_2 \rangle \} \\ &\quad + K_3 \langle I_g \rangle \{ \lambda_1^2 \lambda_2^2 \langle I_1 \rangle \langle I_2 \rangle + \lambda_2^2 \lambda_3^2 \langle I_2 \rangle \langle I_3 \rangle \\ &\quad + \lambda_1^2 \lambda_3^2 \langle I_1 \rangle \langle I_3 \rangle \} + K_3 \lambda_1^2 \lambda_2^2 \lambda_3^2 \langle I_1 \rangle \langle I_2 \rangle \langle I_3 \rangle.\end{aligned}$$

I_1, I_2, I_3 are the values of I_s for special positions involving, respectively, two, one and none (fixed positions) of the variables θ, φ, ψ , and $\lambda_1, \lambda_2, \lambda_3$ are the corresponding constants λ defined as in Table 2.

The value of K_1 is 6 for centrosymmetrical and 4 for non-centrosymmetrical plane groups and space groups, the value of K_2 is 15 for centrosymmetrical and 9 for noncentrosymmetrical plane groups and space groups, and the value of K_3 is 90 for centrosymmetrical and 36 for non-centrosymmetrical plane groups and space groups.

If the special positions are fixed points, with no variable parameters, none of the expressions in Table 1 is appropriate. It is then usually necessary, with a single set of equivalent fixed points, to divide the reflexions into two groups. For one group half the atoms at fixed points scatter in phase with respect to each other but out of phase with respect to the other half so that $\langle I_s^r \rangle = 0$; for the other group all the atoms scatter in phase and we have $\langle I_s^r \rangle = f_s^{2r}$.

If there are several non-equivalent fixed points the relative phases have to be considered in more detail and we then use

$$\langle I_s^r \rangle = (\alpha_1 f_1 + \alpha_2 f_2 + \dots + \alpha_n f_n)^{2r},$$

where f_1, f_2, \dots, f_n are the scattering factors of atoms at the non-equivalent fixed points 1, 2, ..., n , and $\alpha_n = 0, +1$ or -1 ; the appropriate values of α_n are obtained from the geometrical structure factor on introducing the coordinates of the fixed points.

The foregoing treatment will be adequate, in practice, for most triclinic, monoclinic and orthorhombic crystals containing atoms in special positions. But modifications may be required when atoms occupy more than one type of special position. The most general problem arises when A and B involve all three variables θ, φ and ψ , and when some atoms are in general positions, some occupy special positions involving two variables, some occupy special positions involving only one variable, and some occupy fixed positions. Table 2 is then replaced by Table 3.

3. Comparison of experimental and theoretical moments

The experimental data are usually available in the form of relative intensities to which have been applied Lorentz-polarization factors and such corrections as those for absorption. Accidentally absent reflexions must be included in the analysis but systematically absent reflexions are omitted; reflexions with $\sin \theta \leq \lambda$ (shortest cell dimension) are also omitted for theoretical reasons (Wilson, 1949). When working with three-dimensional data it is usually necessary to omit reflexions with one or two indices zero since in general their structure-factor formulae and, therefore, their moments are different from those of general reflexions hkl ; similarly, reflexions with two indices zero are omitted from two-dimensional data.

Since neither the absolute scale factor nor the isotropic temperature factor, $\exp(-2B \sin^2 \theta / \lambda^2)$, is known, it is convenient to work in terms of the function z which is independent of these parameters. Procedures for determining the $\langle I \rangle$ curve required for the derivation of experimental values of z have been described by Howells, Phillips & Rogers (1950) and the effects of errors in this curve have been discussed by Rogers, Stanley & Wilson (1955). We have usually divided the reflexions into about half a dozen (j) groups, each covering a small range of θ , and determined $\langle I \rangle_j$ for each of these groups; with two-dimensional data it may be necessary to increase the number of reflexions in each range by using reflexions more than once in overlapping ranges. Values of z for each reflexion are then given with sufficient accuracy by $I/\langle I \rangle_j$. The second, third and higher moments of z are obtained, respectively, from the average values of z^2, z^3, z^4, \dots .

When the material giving rise to the X-ray re-

flexions consists of more than one type of atom, the moments of z will be θ -dependent because of the variation with θ in the relative magnitudes of the scattering factors for different atoms. It may then be necessary to divide the reflexions into a few ranges of θ — the ranges used in calculating the experimental moments are often convenient though usually narrower than strictly required — and to determine the theoretical moments at a value of θ corresponding to the centre of each range. Theoretical and experimental moments may then be compared in each range or they may be compared for the entire set of reflexions by weighting the moments in each range with the number of reflexions in that range. With many materials, particularly organic compounds containing only carbon, nitrogen, oxygen and hydrogen (which can be neglected), the constituent atoms are sufficiently similar in scattering power for the θ -variation in moments to be negligible; if the theoretical moments are found to be effectively constant at three or four widely separated values of θ , then it is clear that the experimental moments can be derived from the outset for the whole set of reflexions. This point is discussed further in § 4, example (i).

In practice we have found that it is usually quite sufficient to compare theoretical and experimental values of $\langle z^2 \rangle$, though we have usually compared values of $\langle z^3 \rangle$ also, as a check. Occasionally we have compared values of $\langle z^4 \rangle$, but since the results for fourth moments have never been at variance with those obtained from second and third moments, and since the computations become more tedious for higher moments, we have omitted expressions for $\langle I^4 \rangle$ from this paper.

4. Examples

Moment tests have been carried out successfully on several materials examined in this department. In the three examples described here the tests helped to determine space groups which were unknown at the time the tests were made.

(i) 9-*p*-Ethoxycarbonylphenyl-9-stibafluorene

The 2 molecules of $C_{20}H_{17}O_2.Sb$ in the triclinic unit cell (Chaudhuri, 1955) must occupy general positions and the problem was to distinguish between $P1$ and $P\bar{1}$.

$P1$:

The geometrical structure factor for reflexions hkl is

$$A = \cos 2\pi(hx + ky + lz); \quad B = \sin 2\pi(hx + ky + lz).$$

A and B retain the same form for the $0kl$ and $hk0$ reflexions examined, hence the first set of expressions in Table 1 gives the theoretical moments:

$$\begin{aligned} \langle I \rangle &= S(2) \\ \langle I^2 \rangle &= 2S^2(2) - S(4) \\ \langle I^3 \rangle &= 6S^3(2) - 9S(2)S(4) + 4S(6), \end{aligned}$$

Table 4. Comparison of experimental and theoretical moments of z for 9-*p*-ethoxycarbonylphenyl-9-stibafluorene

	sin θ range	Number of reflexions	$\langle z^2 \rangle$			$\langle z^3 \rangle$		
			Experimental	Theoretical $P1$	Theoretical $P\bar{1}$	Experimental	Theoretical $P1$	Theoretical $P\bar{1}$
$hk0$	0.20-0.38	29	1.82	1.21	1.80	4.5	1.70	4.20
	0.38-0.50	29	1.83	1.16	1.74	3.9	1.50	3.78
	0.50-0.70	71	1.98	1.16	1.74	4.2	1.50	3.78
	0.70-0.85	62	2.69	1.16	1.74	7.2	1.50	3.78
	0.85-1.00	55	1.75	1.18	1.76	3.6	1.55	3.95
	Weighted average values for all reflexions		2.07	1.17	1.75	4.8	1.54	3.87
$0kl$	0.20-0.38	25	1.88	1.21	1.81	4.6	1.70	4.25
	0.38-0.48	24	1.46	1.16	1.74	3.2	1.50	3.78
	0.48-0.65	48	3.94	1.16	1.74	13.2	1.50	3.78
	0.65-0.75	50	1.72	1.16	1.74	3.9	1.50	3.78
	0.75-1.00	48	2.13	1.17	1.75	5.1	1.55	3.85
	Weighted average values for all reflexions		2.35	1.17	1.75	6.4	1.54	3.86
	Wilson (1949) distribution		2	3		6	15	

whence

$$\langle z^2 \rangle = \langle I^2 \rangle / \langle I \rangle^2 = 2 - S(4) / S^2(2)$$

and

$$\langle z^3 \rangle = \langle I^3 \rangle / \langle I \rangle^3 = 6 - 9S(4) / S^2(2) + 4S(6) / S^3(2).$$

$P\bar{1}$:

Similarly when $A = \cos 2\pi(hx + ky + lz)$; $B = 0$ we obtain, using the second set of expressions in Table 1,

$$\langle z^2 \rangle = 3 - 3S(4) / 2S^2(2)$$

and

$$\langle z^3 \rangle = 15 - 45S(4) / 2S^2(2) + 10S(6) / S^3(2).$$

Experimental moments, calculated from observed intensities for several ranges of $\sin \theta$ (Cu K radiation), are compared in Table 4 with the theoretical moments calculated at the centre of each range. The weighted average values, and those for nearly all the individual ranges, indicate clearly that the space group is $P\bar{1}$.

It will be seen that the experimental moments tend to be higher than the theoretical moments. This may be due to errors in evaluating the $\langle I \rangle$ function (Rogers, Stanley & Wilson, 1955) — the data used here are not corrected for absorption errors, which are known to be large — or to hypersymmetry (Rogers & Wilson, 1953; Wilson, 1956); both of these effects increase the values of the experimental moments.

The last line in Table 4 gives theoretical moments for the Wilson (1949) distribution corresponding to a large number of atoms of equal weight. It is interesting to note that if the large contribution of the heavy antimony atom had been ignored and these moments had been compared with the experimental values, then the space group would have been wrongly chosen as $P1$.

Below $\sin \theta = 0.20$ the theoretical moments change rapidly because of sharp changes in the relative values of the scattering factors for light and heavy

atoms, but experimental moments in this range have not been considered for theoretical reasons (Wilson, 1949). The theoretical moments in Table 4 are reasonably constant and it can be seen that the weighted average values differ very little from the values near the centre of the range ($\sin \theta \sim 0.6$). It is easily shown that when there are effectively only two types of atom — as in the present example, where oxygen can be regarded as equivalent to carbon and the hydrogen contribution is negligible — then all moments of z derived from Table 1 can be expressed in terms of the ratio between the scattering factors of the two types of atom (f_{sb}/f_c); the variations of the actual scattering factors with $\sin \theta$ are not important except in so far as they affect this ratio. If there is not much difference between the theoretical moments for the maximum and minimum value of this ratio, then clearly there is no need to group the reflexions, as we have done here, into several different ranges of $\sin \theta$. In the next two examples we have found that the changes in theoretical moments with $\sin \theta$ are, proportionately, even smaller than in the present example. The results are presented, therefore, with all the reflexions grouped into a single range.

(ii) Thiourea dioxide

The space group was still doubtful after an examination of the structure by two-dimensional methods. Moment tests with full hkl data were then used to distinguish between the two possible space groups $P2_1nb$ and $Pmnb$; a three-dimensional structure determination (Sullivan & Hargreaves, 1962) confirmed that the correct space group had been chosen.

X-ray data and dimensional considerations indicate that the 4 molecules of $(H_2N)_2CSO_2$ in the unit cell must either occupy general positions in the space group $P2_1nb$ or lie across the mirror planes in the space group $Pmnb$. Moment calculations for $P2_1nb$ are similar to those given in the previous example, but

the calculations for $Pmnb$ are more complicated because the sulphur and carbon atoms occupy special positions.

The geometrical structure factors for $Pmnb$ are:

$$h=2n, (k+l)=2n \\ A = 8 \cos 2\pi hx \cdot \cos 2\pi ky \cdot \cos 2\pi lz; B=0$$

$$h=2n, (k+l)=2n+1 \\ A = -8 \cos 2\pi hx \cdot \sin 2\pi ky \cdot \sin 2\pi lz; B=0$$

$$h=2n+1, (k+l)=2n \\ A = -8 \sin 2\pi hx \cdot \sin 2\pi ky \cdot \cos 2\pi lz; B=0$$

$$h=2n+1, (k+l)=2n+1 \\ A = -8 \sin 2\pi hx \cdot \cos 2\pi ky \cdot \sin 2\pi lz; B=0.$$

For the atoms in general positions — oxygen, nitrogen and hydrogen — the quantities $\langle I_g^r \rangle$ are evaluated, therefore, using the seventh set of expressions in Table 1.

For the atoms in special positions — sulphur and carbon — on the mirror planes at $x=\frac{1}{4}$ and $x=\frac{3}{4}$, the terms involving x in the structure factors are always unity; the fourth set of expressions in Table 1 must be used, therefore, in evaluating $\langle I_s^r \rangle$.

Table 5. Comparison of experimental and theoretical moments of z for thiourea dioxide

Moment	Experimental	Theoretical	
		$P2_1nb$	$Pmnb$
$\langle z^2 \rangle$	3.0	2.1	2.6
$\langle z^3 \rangle$	13.2	6.4	10.4

Moments $\langle I^r \rangle$ are obtained from $\langle I_g^r \rangle$ and $\langle I_s^r \rangle$ using the formulae in Table 2 with $\lambda=\frac{1}{2}$, $K_1=6$ and $K_2=15$. Theoretical moments of z , evaluated in this way for $Pmnb$, are compared in Table 5 with theoretical moments for $P2_1nb$ and with experimental moments calculated from the intensities of 318 hkl reflexions in the range $\sin \theta=0.5$ to 1.0. There is a strong indication that the true space group is $Pmnb$.

(iii) Sodium aluminum sulphate dodecahydrate

In the monoclinic form of sodium alum the unit cell contains 4 molecules of $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and the space group is either $C2/c$ or Cc . An attempt to determine a structure based on $C2/c$ proved unsuccessful (Kumra & Lipson, 1962). Moment tests on 92 $h0l$ reflexions indicate strongly that the space group is Cc .

The calculation of theoretical moments for Cc is similar to that described in the first example since the molecules would occupy general positions in this space group.

In $C2/c$ there are 8 equivalent general positions; therefore the sodium and aluminum atoms must occupy special positions either on symmetry centres or rotation axes; for $h0l$ reflexions these special positions are fixed points. It is assumed that the oxygen atoms are in general positions and simple

Table 6. Comparison of experimental and theoretical moments of z for sodium alum

Moment	Experimental	Cc	Theoretical	
			(i) $C2/c$	(ii) $C2/c$
$\langle z^2 \rangle$	1.84	1.89	2.61	2.60
$\langle z^3 \rangle$	4.63	5.10	10.0	10.1

In (i) $C2/c$ the sodium and aluminum atoms scatter in phase for all reflexions; in (ii) $C2/c$ they scatter in phase when $(h+l)=4n$ and out of phase when $(h+l)=4n+2$.

stereochemical considerations show that the sulphur atoms must also occupy general positions. Moments $\langle I^r \rangle$ are obtained from $\langle I_g^r \rangle$ and $\langle I_s^r \rangle$ as in the previous example with the difference that there are now two possible sets of expressions for $\langle I_s^r \rangle$. With certain pairs of fixed points the sodium and aluminum atoms scatter in phase for all reflexions in which case

$$\langle I_s^r \rangle = (f_{\text{Na}} + f_{\text{Al}})^{2r}.$$

But with other pairs of fixed points we have

$$\langle I_s^r \rangle = (f_{\text{Na}} + f_{\text{Al}})^{2r} \quad \text{when } (h+l)=4n,$$

and

$$\langle I_s^r \rangle = (f_{\text{Na}} - f_{\text{Al}})^{2r} \quad \text{when } (h+l)=4n+2.$$

The results of the calculations, giving a clear indication that the correct space group is Cc , are presented in Table 6.

5. Discussion

Moment tests have proved to be successful in all the examples of symmetry determination which we have studied and they have resolved problems which could not have been attempted with the usual statistical tests (*International Tables for X-ray Crystallography*, 1952, 1959). They are of particular value under conditions for which the Wilson (1949) probability distributions of X-ray intensities are not valid, *e.g.* when the unit cell contains a small number of atoms, an outstandingly heavy atom or some atoms in special positions. As an examination of the expressions for moments of z indicates, the departures from the Wilson (1949) distributions are greatest when the unit cell contains one atom only or, what is effectively equivalent, one outstandingly heavy atom. The first example in §4 shows that in these circumstances tests based on the Wilson (1949) distributions may lead to completely false conclusions.

Moment tests can also be carried out, of course, on materials for which the Wilson (1949) distributions are applicable. For such materials there is no need to calculate theoretical moments since in all cases they reduce to $\langle z^2 \rangle=2$, $\langle z^3 \rangle=6$ for non-centrosymmetrical plane groups and space groups and $\langle z^2 \rangle=3$, $\langle z^3 \rangle=15$ for centrosymmetrical plane groups and space groups.

Of the alternative statistical tests referred to in *International Tables for X-ray Crystallography* (1952,

1959) only the average-multiple test (Wilson, 1950) can be applied when the material consists of atoms of different weights. Moreover, the scope of the latter test is fairly restricted because it cannot be used to detect centres of symmetry — except, sometimes, indirectly — and because it involves types of reflexions which are frequently too small in number to give statistically significant results.

Wherever possible, moment tests — and, indeed, other statistical tests — should be performed with three-dimensional (hkl) reflexions rather than reflexions with one or two indices zero. The larger number of reflexions available permits more reliable statistical averaging; in addition, the results are less likely to be seriously influenced by hypersymmetry, by the overlap of atoms in projection and by the inadequate statistical averaging which may occur if a heavy atom happens to fall, in projection, near a special position.

When present, hypersymmetry invariably increases the moments of centrosymmetrical structures, but since statistical tests are usually made on unknown structures it is, in general, impossible to allow for hypersymmetry quantitatively.

Overlap may raise or lower moments, depending upon the space group, but the errors which it introduces are likely to be important only with one-dimensional data, or two-dimensional data from

crystals with unit cells containing a small number of atoms or one very heavy atom.

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The Secondary Extinction Correction

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It is shown that Darwin's formula for the secondary extinction correction, which has been universally accepted and extensively used, contains an appreciable error in the X-ray diffraction case. The correct formula is derived.

As a first order correction for secondary extinction Darwin showed that one should use an effective absorption coefficient $\mu + gQ$ where an unpolarized incident beam is presumed. The new derivation shows that the effective absorption coefficient is $\mu + 2gQ(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)^2$, which gives $\mu + gQ$ at $\theta = 0^\circ$ and $\theta = 90^\circ$, but $\mu + 2gQ$ at $\theta = 45^\circ$.

Darwin's theory remains valid when applied to neutron diffraction.

Introduction

The effect of secondary extinction on the integrated intensity of X-ray diffraction in mosaic crystals was first studied in detail by C. G. Darwin (1922), and the formulas derived by him have been used extensively throughout the last forty years.

Recently this writer found that the Darwin equations did not give agreement with precise intensity measurements. As a consequence a reexamination of

the theory was undertaken. It was found that the polarization of the X-ray beams was incorrectly treated in Darwin's paper and in all subsequent theoretical work on secondary extinction. The correct formulas have been derived and have been found to give agreement with experiment. Since the new theoretical treatment of secondary extinction requires significant modifications of equations in general use, the results of the reexamination will be given in some detail in the present article.