

The Use of Moments of X-ray Intensity in Space-Group Determination

I. Derivation of Theoretical Moments

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A comparison of theoretical and experimental moments of the intensities of X-ray reflexions from a crystal provides a test for the crystal symmetry that can be used in conditions for which other statistical tests for symmetry are invalid. Part I is an account of methods for deriving theoretical moments which can be applied to a wide variety of problems.

1. Introduction

Several statistical tests have been developed and used for the detection of symmetry elements in crystals since Wilson (1949) showed that the probability distributions of the intensities of X-ray reflexions are different for centrosymmetric and non-centrosymmetric crystals. A summary of these tests and references to the more important papers are given in *International Tables for X-ray Crystallography* (1959). Most of the tests have been developed on the assumption that the unit cell contains a large number of crystallographically independent atoms of equal weight distributed at random throughout the unit cell. The modifications required when the atoms are not distributed at random have been considered extensively (Lipson & Woolfson, 1952; Rogers & Wilson, 1953; Wilson, 1956; Herbstein & Schoening, 1957) but those required when the atoms are small in number, or differ in weight, or occupy both general and special positions, have received less attention. It has been shown that the latter problem is an important one (Hargreaves, 1955) because an outstandingly heavy atom — such as is often deliberately introduced into a molecule to simplify the structure determination — may modify the probability distribution of X-ray intensities for a centrosymmetrical structure so that it approximates more closely to the Wilson distribution for a non-centrosymmetrical structure with atoms of equal weight than to the distribution for a centrosymmetrical structure with atoms of equal weight. But when the crystal consists of atoms of different weights even an approximate evaluation of the distribution is difficult (Karle & Hauptman, 1953; Hauptman & Karle, 1953; Klug, 1958) and the problem is complicated because the distribution then depends upon the presence or absence of other symmetry elements besides centres; in general, each space group or plane group has to be considered separately.

Statistical tests for crystal symmetry, which are valid when both light and heavy atoms are present, have been devised for certain rather special cases

(Hargreaves, 1955, 1956; Collin, 1955; Sim, 1958*a, b*) but it is desirable that a test should be available which can be applied to a wide variety of distributions. It is the aim of this paper (Part I) and the succeeding one (Part II; Foster & Hargreaves, 1963) to show that a comparison of theoretical and experimental moments of intensity is suitable for this purpose.

Part I is an account of a procedure for deriving theoretical expressions for moments of intensity for any numbers and relative weights of atoms in crystals with triclinic, monoclinic and orthorhombic space groups; special positions and hypersymmetry can be taken into consideration. Part II, which is concerned with the practical application of these results in the determination of space group symmetry, is presented so that it can be used without reference to the theory developed in the present paper.

In practice it is convenient to express each intensity I_θ as a fraction, z_θ , of the local average intensity $\langle I \rangle_\theta$ (Howells, Phillips & Rogers, 1950) and to compare theoretical and experimental moments of $z_\theta = I_\theta / \langle I \rangle_\theta$.

The second moment of z , $\langle z^2 \rangle$, is related to the specific variance v , by the equation

$$\langle z^2 \rangle = v + 1. \quad (1)$$

Wilson (1951) has advocated the use of the variance test for crystals with a small number of atoms, or dominating heavy atoms, in the unit cell. Under the latter conditions, however, the variance depends upon the space group symmetry whereas Wilson has derived theoretical expressions for two cases only, *viz.* crystals with no symmetry and those with only centrosymmetry. Our results confirm those of Wilson and extend them to a much wider range of symmetries.

2. Random variable theory

2.1. The r th moment of intensity, $\langle I^r \rangle$, is calculated for n experimentally observed intensities $I(hkl)$ from

$$\langle I^r \rangle = \sum_{hkl} \frac{I^r(hkl)}{n}. \quad (2)$$

For the present argument it will be assumed that $I(hkl)$ are on the absolute scale and that the atomic scattering factors f_i are effectively constant for all reflexions within the group. Equation (2) can then be written in terms of the structure factors $F(hkl)$ as

$$\langle F^{2r} \rangle = \sum_{hkl} \frac{F^{2r}(hkl)}{n}. \quad (3)$$

$F(hkl)$ consists of series of terms of the type $\cos 2\pi hx_i$, $\cos 2\pi ky_i$, $\cos 2\pi lz_i$, $\sin 2\pi hx_i$, $\sin 2\pi ky_i$ and $\sin 2\pi lz_i$, where x_i , y_i and z_i ($i=1, 2 \dots m$) are atomic coordinates, and if these coordinates were known we could calculate the sum in equation (3).

As a simple illustration consider two atoms, related by a twofold axis, for which $F(h) = 2f \cos 2\pi hx$. Now $\cos^{2r} 2\pi hx$ can be represented by the series

$$\begin{aligned} \cos^{2r} 2\pi hx &= \langle \cos^{2r} \theta \rangle + a_4 \cos 4\pi hx \\ &\quad + a_8 \cos 8\pi hx + \dots a_{4r} \cos 4r\pi hx, \end{aligned}$$

where θ is a random variable uniformly distributed in the range $(0-2\pi)$ and, therefore,

$$\langle F^{2r} \rangle = 2^{2r} f^{2r} \left\{ \langle \cos^{2r} \theta \rangle + \frac{1}{n} \left(a_4 \sum_{h=1}^n \cos 4\pi hx + \dots a_{4r} \sum_{h=1}^n \cos 4r\pi hx \right) \right\}. \quad (4)$$

Since

$$\sum_{h=1}^n \cos 2\pi hx = \frac{1}{2} \left\{ \frac{\sin (2n+1)\pi x}{\sin \pi x} - 1 \right\}$$

we can write equation (4) as

$$\langle F^{2r} \rangle = 2^{2r} f^{2r} \langle \cos^{2r} \theta \rangle + f^{2r} R(nx)/n. \quad (5)$$

Now because $R(nx)$ is a bounded oscillating function of n , $R(nx)/n$ is a convergent oscillating sequence which tends to zero as n tends to infinity; thus for large n the experimental moment will approximate to the value which would be obtained by considering $2\pi hx$ to be a uniformly distributed random variable, θ . A general structure factor could in principle be treated similarly leading to an expression of the form

$$\langle F^{2r} \rangle = \langle F^{2r}(\theta_i, \varphi_i, \psi_i) \rangle + B, \quad (6)$$

where the first term on the right-hand side is the moment obtained by replacing all arguments of the form $2\pi hx_i$, $2\pi ky_i$ and $2\pi lz_i$ by the random variables θ_i , φ_i and ψ_i , and B is a bounded function which tends to small values as the number of values h , k and l becomes large. The problem of calculating the value of B from x_i , y_i and z_i is, in general, very difficult, and for practical purposes it is impossible because the atomic coordinates are unknown at the stage in crystal structure determination when a statistical analysis is needed. In practice, B is usually small for a reasonable number of reflexions and it is sufficient for our purpose to calculate the first term on the right of equation (6). The first step, therefore,

in the calculation of theoretical moments of intensity is to make the substitutions

$$2\pi hx_i = \theta_i, \quad 2\pi ky_i = \varphi_i \quad \text{and} \quad 2\pi lz_i = \psi_i, \quad (7)$$

θ_i , φ_i and ψ_i being subsequently treated as independent random variables which are uniformly distributed over the range $(0-2\pi)$. It follows that the joint probability distribution of θ_i , φ_i and ψ_i is of the form $1/(2\pi)^3$ and

$$\langle F^{2r} \rangle = \int_{\theta_1=0}^{2\pi} \dots \int_{\theta_m=0}^{2\pi} \int_{\varphi_1=0}^{2\pi} \dots \int_{\varphi_m=0}^{2\pi} \int_{\psi_1=0}^{2\pi} \dots \int_{\psi_m=0}^{2\pi} F^{2r} \prod_{i=1}^m \frac{d\theta_i d\varphi_i d\psi_i}{(2\pi)^3}. \quad (8)$$

2.2. The substitution process of equations (7) is trivial for structure factors of the triclinic, monoclinic and orthorhombic space groups because independence of arguments is obvious, but for higher symmetries some care is needed.

Consider, for example, the geometrical structure factor for the plane group $p6$,

$$\begin{aligned} A &= \cos 2\pi(hx + ky) + \cos 2\pi(kx - \{h+k\}y) \\ &\quad + \cos 2\pi(hy - \{h+k\}x), \end{aligned} \quad (9)$$

for which independence of arguments is not obvious, and which can be written as

$$A = \cos \alpha + \cos \beta + \cos \gamma.$$

An examination of equation (9) reveals the linear relation $\alpha + \beta + \gamma = 0$ and, therefore,

$$A = \cos \alpha + \cos \beta + \cos (\alpha + \beta). \quad (10)$$

It must now be shown, if possible, that α and β are independent, uniformly distributed in the range $(0-2\pi)$ and that, as for the triclinic, monoclinic and orthorhombic space groups, the moments are independent of h and k . This property of the moments can be established for the present example (Appendix 4) but it does not always hold for space groups in the systems of high symmetry.

Finally, consider the plane group $p4m$ for which

$$F = \sum_{i=1}^n f_i (\cos 2\pi hx_i \cos 2\pi ky_i + \cos 2\pi kx_i \cos 2\pi hy_i). \quad (11)$$

No transformation can be found such that the random variables are independent of all h and k . To calculate moments we must specify some relation between h and k , say $k = \lambda h$. The structure-factor expression then becomes

$$F = \sum_{i=1}^n f_i (\cos \theta_i \cos \lambda \varphi_i + \cos \lambda \theta_i \cos \varphi_i), \quad (12)$$

the moments of which depend upon the value of λ . Therefore in comparing theoretical and experimental moments we must sample only those reflexions for which $k = \lambda h$.

The considerations which are illustrated in § 2·2 must be applied to the structure factor expressions for all the more complex symmetries; that is, the expressions must be put in a form containing only independent variables and dependence on indices must be determined before moments are calculated.

3. Derivation of moments: atoms in general positions

3·1. We shall derive moments for the intensity scattered by the asymmetric unit in the unit cell. The resulting moments would need to be multiplied by suitable integers to put them on the absolute scale, but these integers are eliminated when moments of intensity are converted to moments of z (§ 1). Consideration of the asymmetric unit, rather than the complete unit cell, greatly simplifies the application of the results derived in Part I to a systematic study of a wide variety of space groups (Part II: Foster & Hargreaves, 1963).

Let the structure factor for an asymmetric unit containing n atoms be represented by

$$F = \sum_1^n f_i \xi_i + j \sum_1^n f_i \eta_i, \quad (13)$$

where ξ_i and η_i are, in general, trigonometrical functions of the independent variables θ_i , φ_i and ψ_i . For convenience the element of volume $d\theta_i d\varphi_i d\psi_i / (2\pi)^3$ will be denoted by dV_i and integrals of the type

$$\int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \alpha(\theta_i, \varphi_i, \psi_i) \frac{d\theta_i d\varphi_i d\psi_i}{(2\pi)^3}$$

will be written as

$$\int_{V_i} \alpha dV_i.$$

On writing equation (13) as $F = A + jB$ the r th moment of intensity is given by

$$\langle I^r \rangle = \int_{V_1} \dots \int_{V_n} (A^2 + B^2)^r \prod_{i=1}^n dV_i \quad (14)$$

and, therefore, on expanding the integrand by the binomial theorem we have

$$\langle I^r \rangle = \sum_{s=0}^r \frac{r!}{s! (r-s)!} M_{2s, 2(r-s)}. \quad (15)$$

The quantity M_{pq} (p and q even) in equation (15) will be referred to as the partial moment of order pq for the asymmetric unit. From equations (14) and (15) it follows that

$$M_{pq} = \int_{V_1} \dots \int_{V_n} A^p B^q \prod_{i=1}^n dV_i = \int A^p B^q dV. \quad (16)$$

Similarly we define the partial moment for one atom by

$$m_{pq} = \int_{V_i} \xi^p \eta^q dV_i. \quad (17)$$

The moments M_{pq} can be derived by separating the series $A^p B^q$ into terms which are either zero or non-zero on integration. For convenience of manipulation of the series involved we shall use the following notation:

$$\sum_{i=1}^n a_i^\alpha = a_1^\alpha + a_2^\alpha + \dots + a_n^\alpha$$

will be denoted by $S(\alpha)$ and

$$\sum_{i=1}^n b_i^\alpha,$$

where b_i is not a member of the set a_i , will be denoted by $S(\alpha^1)$. The double series

$$\begin{aligned} \sum_{i \neq j} a_i^{\alpha_1} a_j^{\alpha_2} &= \sum_{i=1}^n (a_i^{\alpha_1} \sum_{j \neq i} a_j^{\alpha_2}) \\ &= a_1^{\alpha_1} (a_2^{\alpha_2} + a_3^{\alpha_2} + \dots + a_n^{\alpha_2}) + a_2^{\alpha_1} (a_1^{\alpha_2} + a_3^{\alpha_2} + \dots + a_n^{\alpha_2}) \\ &\quad + a_n^{\alpha_1} (a_1^{\alpha_2} + a_2^{\alpha_2} + \dots + a_{n-1}^{\alpha_2}) \end{aligned}$$

will be denoted by $S(\alpha, \beta)$ and, in general, the m -tuple series

$$\sum_{i_1=1}^n \sum_{i_2=1}^n \dots \sum_{i_m=1}^n a_{i_1}^{\alpha_1} a_{i_2}^{\alpha_2} \dots a_{i_m}^{\alpha_m} \quad (i_1 \neq i_2 \neq \dots \neq i_m)$$

will be denoted by $S(\alpha_1, \alpha_2, \dots, \alpha_m)$ and

$$\sum_{i_1=1}^n \sum_{i_2=1}^n \dots \sum_{i_m=1}^n a_{i_1}^{\alpha_1} b_{i_1}^{\beta_1} a_{i_2}^{\alpha_2} \dots a_{i_m}^{\alpha_m} \quad (i_1 \neq i_2 \neq \dots \neq i_m)$$

by $S(\alpha_1 \beta^1, \alpha_2, \alpha_3, \dots, \alpha_m)$.

Since the m -tuple series consist of the sums of terms of type

$$a_{i_1}^{\alpha_1} a_{i_2}^{\alpha_2} \dots a_{i_m}^{\alpha_m} \quad \text{or} \quad a_{i_1}^{\alpha_1} b_{i_1}^{\beta_1} a_{i_2}^{\alpha_2} \dots a_{i_m}^{\alpha_m}$$

we can, from symmetry considerations, permute the letters separated by commas in the brackets in any way we please: thus $S(\alpha, \beta) = S(\beta, \alpha)$; $S(\alpha, \beta, \gamma) = S(\beta, \alpha, \gamma) = S(\gamma, \alpha, \beta)$; $S(\alpha_2 \beta^1, \alpha_3) = S(\alpha_3, \alpha_2 \beta^1)$ etc.

The rules for multiplying series are derived in Appendix I.

3·2. *Integration of S .* We can write equation (13) as

$$F = S_T(1) + jS_T(1^1), \quad (18)$$

where the suffix T denotes that the series contains

trigonometric factors. We will denote the series $\sum_{i=1}^n f_i^\alpha$

by $S(\alpha)$. Now $S_T(\alpha_1, \alpha_2, \dots, \alpha_m)$ consists of terms

$$f_{i_1}^{\alpha_1} f_{i_2}^{\alpha_2} \dots f_{i_m}^{\alpha_m} \xi_{i_1}^{\alpha_1} \xi_{i_2}^{\alpha_2} \dots \xi_{i_m}^{\alpha_m}$$

which become, on integration,

$$m_{\alpha_1 0} \cdot m_{\alpha_2 0} \dots m_{\alpha_m 0} f_{i_1}^{\alpha_1} f_{i_2}^{\alpha_2} \dots f_{i_m}^{\alpha_m}$$

and therefore

$$\begin{aligned} \int S_T(\alpha_1, \alpha_2, \dots, \alpha_m) dV \\ = m_{\alpha_1 0} \cdot m_{\alpha_2 0} \dots m_{\alpha_m 0} S(\alpha_1, \alpha_2, \dots, \alpha_m). \end{aligned} \quad (19)$$

Similarly,

$$\int S_T(\alpha_1^1, \alpha_2^1, \dots, \alpha_m^1) dV = m_{0\alpha_1} \cdot m_{0\alpha_2} \dots m_{0\alpha_m} S(\alpha_1, \alpha_2, \dots, \alpha_m),$$

and

$$\int S_T(\alpha_1\beta_1^1, \alpha_2\beta_2^1, \dots) dV = m_{\alpha_1\beta_1} \cdot m_{\alpha_2\beta_2} \dots S(\alpha_1 + \beta_1, \alpha_2 + \beta_2, \dots)$$

and, in general,

$$\int S_T(\alpha_1\beta_1^1, \alpha_2\beta_2^1, \dots, \gamma_1, \gamma_2, \dots, \delta_1^1, \delta_2^1, \dots) dV = m_{\alpha_2\beta_1} \cdot m_{\alpha_2\beta_2} \dots m_{\gamma_1 0} \cdot m_{\gamma_2 0} \dots m_{0\delta_1} \cdot m_{0\delta_2} \dots S(\alpha_1 + \beta_1, \alpha_2 + \beta_2, \dots, \gamma_1, \gamma_2, \dots, \delta_1, \delta_2, \dots) \tag{20}$$

the primes vanishing because the distinction between the terms for the real and imaginary parts does not exist after integration.

For the triclinic, monoclinic and orthorhombic space groups the partial moments m_{pq} are zero when either p or q is odd, but for higher symmetries non-zero moments exist for p odd and q even: in addition m_{10} and m_{01} are zero for all symmetries. M_{pq} exist, for moments of intensity, only when both p and q are even (equation (15)): by equations (16) and (18) they are given by

$$M_{p0} = \int S_T^p(1) dV. \tag{21}$$

$$M_{pq} = \int S_T^p(1) S_T^q(1^1) dV. \tag{22}$$

3.3. Partial moments M_{p0} . The series expansions of $S^r(1)$ for $r=1, 2, \dots, 8$ are given in Appendix II. To illustrate the method of using these series we shall derive M_{60} .

By equation (21)

$$M_{60} = \int S_T^6(1) dV,$$

whence, using equation (A14),

$$\begin{aligned} M_{60} = & \int S_T(6) dV + 6 \int S_T(5, 1) dV + 10 \int S_T(3, 3) dV \\ & + 15 \int S_T(2, 4) dV + 60 \int S_T(3, 2, 1) dV \\ & + 20 \int S_T(3, 1, 1, 1) dV + 15 \int S_T(4, 1, 1) dV \\ & + 15 \int S_T(2, 1, 1, 1, 1) dV \\ & + 45 \int S_T(2, 2, 1, 1) dV + 15 \int S_T(2, 2, 2) dV \\ & + \int S_T(1, 1, 1, 1, 1, 1) dV \end{aligned}$$

and therefore from equation (19), and omitting terms containing m_{10} , which is zero, we obtain

$$M_{60} = m_{60} S(6) + 10m_{30}^2 S(3, 3) + 15m_{20}m_{40} S(2, 4) + 15m_{20}^3 S(2, 2, 2).$$

Now, as in § A1.4 (Appendix I) and using equation (A4), we derive the relations

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

and

$$S(3, 3) = S^2(3) - S(6),$$

whence,

$$M_{60} = 15m_{20}^3 S^3(2) + \{15m_{20}m_{40} - 45m_{20}^3\} S(2) \cdot S(4) + 10m_{30}^2 S^2(3) + \{m_{60} + 30m_{20}^2 - 15m_{20}m_{40} - 10m_{30}^2\} S(6).$$

3.4. Partial moments M_{pq} . As an example we shall derive M_{24} .

By equation (22),

$$M_{24} = \int S_T^2(1) S_T^4(1^1) dV$$

whence, using equations (A10) and (A12),

$$\begin{aligned} M_{24} = & \int \{S_T(2) + S_T(1, 1)\} \{S_T(4^1) + 4S_T(3^1, 1^1) \\ & + 6S_T(2^1, 1^1, 1^1) + 3S_T(2^1, 2^1) \\ & + S_T(1^1, 1^1, 1^1, 1^1)\} dV. \tag{23} \end{aligned}$$

Now by equations (A7) and (20) we have, for multiplications involving a *single* series,

$$\begin{aligned} \int S_T(2) S_T(4^1) dV &= \int S_T(24^1) dV + \int S_T(2, 4^1) dV \\ &= m_{24} S(6) + m_{20} m_{04} S(2, 4) \end{aligned}$$

$$\begin{aligned} \int S_T(2) S_T(2^1, 2^1) dV &= 2 \int S_T(22^1, 2^1) dV + \int S_T(2^1, 2^1, 2) dV \\ &= 2m_{22} m_{02} S(4, 2) + m_{02}^2 m_{20} S(2, 2, 2). \end{aligned}$$

$$\begin{aligned} \int S_T(2) S_T(2^1, 1^1, 1^1) dV &= \int S_T(22^1, 1^1, 1^1) dV \\ &+ 2 \int S_T(2^1, 21^1, 1^1) dV + \int S_T(2, 2^1, 1^1, 1^1) dV \\ &= m_{22} m_{01}^2 S(4, 1, 1) + 2m_{02} m_{21} m_{01} S(3, 2, 1) \\ &+ m_{20} m_{02} m_{01}^2 S(2, 2, 1, 1). \end{aligned}$$

The last expression is zero since $m_{10} = m_{01} = 0$ and $m_{pq} = 0$ if q is odd. Similarly the integrals of

$$\begin{aligned} S_T(2) S_T(1^1, 1^1, 1^1, 1^1), & S_T(2) \cdot S_T(3^1, 1^1) \\ & \text{and } S_T(4^1) \cdot S_T(1, 1) \end{aligned}$$

are zero.

For the multiplications of double series we have, as in equation (A8) and by equation (20),

$$\begin{aligned} \int S_T(1, 1) S_T(3^1, 1^1) dV &= 2 \int S_T(3^1 1, 1^1) dV + 2 \int S_T(13^1, 1, 1^1) dV \\ &+ 2 \int S_T(3^1, 11^1, 1) dV + \int S_T(3^1, 1^1, 1, 1) dV \end{aligned}$$

$$\begin{aligned}
 &= 2m_{13}m_{11}S(4, 2) + 2m_{13}m_{10}m_{01}S(4, 1, 1) \\
 &+ 2m_{03}m_{11}m_{10}S(3, 2, 1) + m_{03}m_{01}m_{10}^2S(3, 1, 1, 1). \\
 &\int S_T(1, 1)S_T(2^1, 1^1, 1^1)dV \\
 &= 4 \int S_T(2^1, 11^1, 1^1)dV + 2 \int S_T(2^1, 11^1, 11^1)dV \\
 &+ 2 \int S_T(2^1, 1, 1^1, 1^1)dV \\
 &+ 4 \int S_T(2^1, 11^1, 1, 1^1)dV + \int S_T(2^1, 1^1, 1^1, 1, 1)dV \\
 &= 4m_{12}m_{11}m_{01}S(3, 2, 1) + 2m_{02}m_{11}^2S(2, 2, 2) \\
 &+ 2m_{12}m_{10}m_{01}^2S(3, 1, 1, 1) \\
 &+ 4m_{02}m_{11}m_{10}m_{01}S(2, 2, 1, 1) \\
 &+ m_{02}m_{01}^2m_{10}^2S(2, 1, 1, 1, 1).
 \end{aligned}$$

The last two expressions are zero since $m_{10}=m_{01}=m_{11}=0$ and, by the same considerations, the integral of $S_T(1, 1)S_T(1^1, 1^1, 1^1, 1^1)$ is also zero. The remaining integral,

$$\begin{aligned}
 &\int S_T(1, 1)S_T(2^1, 2^1)dV \\
 &= 2 \int S_T(12^1, 12^1)dV + 4 \int S_T(12^1, 2^1, 1)dV \\
 &+ \int S_T(2^1, 2^1, 1, 1)dV \\
 &= 2m_{12}^2S(3, 3) + 4m_{12}m_{02}m_{10}S(3, 2, 1) \\
 &+ m_{02}^2m_{10}^2S(2, 2, 1, 1),
 \end{aligned}$$

contains one non-zero term, viz. $2m_{12}^2S(3, 3)$. On adding all the non-zero terms in equation (23) we have

$$\begin{aligned}
 M_{24} &= 3m_{20}m_{02}^2S(2, 2, 2) + \{m_{20}m_{04} + 6m_{22}m_{02}\}S(2, 4) \\
 &+ 6m_{12}^2S(3, 3) + m_{24}S(6)
 \end{aligned}$$

which becomes, on using the relationships in § 3·3,

$$\begin{aligned}
 M_{24} &= 3m_{20}m_{02}^2S^3(2) \\
 &+ \{m_{20}m_{04} + 6m_{22}m_{02} - 9m_{20}m_{02}^2\}S(2)S(4) \\
 &+ 6m_{12}^2S^2(3) \\
 &+ \{m_{24} - m_{20}m_{04} - 6m_{22}m_{02} - 6m_{12}^2 + 6m_{20}m_{02}^2\}S(6).
 \end{aligned}$$

3·5. *Partial moments* M_{0r} . M_{0r} are the same as M_{r0} with all m_{r0} replaced by m_{0r} , except that no odd moments exist; for example

$$\begin{aligned}
 M_{06} &= 15m_{02}^3S^3(2) + \{15m_{02}m_{04} - 45m_{02}^3\}S(2)S(4) \\
 &+ \{30m_{02}^3 - 15m_{02}m_{04} + m_{06}\}S(6).
 \end{aligned}$$

3·6. Values of M_{p0} and M_{pq} , calculated by the methods described in § 3·3 and § 3·4, are presented in Appendix III. They are sufficient for evaluating the first four moments of intensity for all space groups in the triclinic, monoclinic and orthorhombic systems and for some, though possibly not all, space groups of higher symmetry. The expressions in Appendix 3 are simplified considerably for triclinic, monoclinic

and orthorhombic space groups for all of which $m_{pq}=0$ when either p or q is odd (§ 3·2): the simplified expressions have been used to evaluate the moments presented in Part II (Foster & Hargreaves, 1963). Space groups of higher symmetry are now under examination.

3·7. *Derivation of moments for P222*. To illustrate the general procedure for deriving expressions for theoretical moments we shall consider the space group P222 for which

$$A = \cos \theta \cos \varphi \cos \psi, \quad B = \sin \theta \sin \varphi \sin \psi.$$

The partial moments m_{pq} are obtained by equation (17), which gives

$$\begin{aligned}
 m_{pq} &= \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \cos^p \theta \sin^q \theta \cos^p \varphi \sin^q \varphi \cos^p \psi \sin^q \psi \\
 &\times \frac{d\theta d\varphi d\psi}{(2\pi)^3}.
 \end{aligned}$$

On integration we obtain the numerical results

m_{20}	m_{02}	m_{22}	m_{40}	m_{04}	m_{42}	m_{24}	m_{60}	m_{06}
$\frac{1}{8}$	$\frac{1}{8}$	$(\frac{3}{8})^3$	$(\frac{3}{8})^3$	$(\frac{3}{8})^3$	$(\frac{1}{16})^3$	$(\frac{1}{16})^3$	$(\frac{5}{16})^3$	$(\frac{5}{16})^3$

in addition, $m_{30}=m_{12}=0$ for an orthorhombic space group (§ 3·2). On substituting these values in the expressions for $M_{20}, M_{02}, M_{22}, M_{40}, M_{04}, M_{42}, M_{24}, M_{60}$ and M_{06} (Appendix III) and using equation (15) we obtain

$$\begin{aligned}
 \langle I \rangle &= \frac{1}{4}S(2) \\
 \langle I^2 \rangle &= \frac{1}{8}S^2(2) - \frac{1}{64}S(4) \\
 \langle I^3 \rangle &= \frac{3}{32}S^3(2) - \frac{9}{256}S(2) \cdot S(4) + \frac{1}{256}S(6).
 \end{aligned}$$

For practical reasons (Foster & Hargreaves, 1963) it is preferable to work in terms of the variable $z = I/\langle I \rangle$ (§ 1) and so, since

$$\langle z^r \rangle = \langle I^r \rangle / \langle I \rangle^r$$

we have, finally,

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

The fourth and higher moments of z can, of course, be derived in a similar way.

The derivation of moment expressions for centrosymmetrical space groups is relatively simple since for such space groups equation (15) reduces to $\langle I^r \rangle = M_{r0}$.

4. Atoms in special positions

4·1. *Centrosymmetrical space groups*. When some atoms are in special positions the most general form which the structure factor can take is

$$F = A \sum_g f_i \alpha_i + B \sum_{s_1} f_i \beta_i + C \sum_{s_2} f_i \gamma_i + D \sum_{s_3} f_i \delta_i, \quad (24)$$

where \sum_g is the summation over the atoms in general positions and \sum_{s_1} , \sum_{s_2} and \sum_{s_3} are the summations over the atoms in the three possible types of special position, *i.e.* with 2, 1 and 0 variables. For our purpose the constants A , B , C and D can be replaced by $\lambda_1 = B/A$, $\lambda_2 = C/A$ and $\lambda_3 = D/A$ because the final moments will be in terms of z ; we shall therefore write equation (24) as

$$F = G + \lambda_1 S_1 + \lambda_2 S_2 + \lambda_3 S_3 \quad (25)$$

giving

$$\langle I^r \rangle = \langle (G + \lambda_1 S_1 + \lambda_2 S_2 + \lambda_3 S_3)^{2r} \rangle. \quad (26)$$

Now the variables θ , φ , and ψ associated with G are different from those associated with S_1 , S_2 and S_3 ; therefore

$$\begin{aligned} \langle G^{2r} (\lambda_1 S_1)^{2t} \rangle &= \langle G^{2r} \rangle \langle \lambda_1^{2t} S_1^{2t} \rangle, \\ \langle (\lambda_1 S_1)^{2r} (\lambda_2 S_2)^{2t} \rangle &= \langle (\lambda_1 S_1)^{2r} \rangle \langle (\lambda_2 S_2)^{2t} \rangle \text{ etc.} \end{aligned}$$

which we represent by

$$\lambda_1^{2t} \langle I_g^r \rangle \langle I_1^t \rangle, \lambda_1^{2r} \lambda_2^{2t} \langle I_1^r \rangle \langle I_2^t \rangle \text{ etc.}$$

On putting $r=1$ in equation (26) we have

$$\langle I \rangle = \langle I_g \rangle + \lambda_1^2 \langle I_1 \rangle + \lambda_2^2 \langle I_2 \rangle + \lambda_3^2 \langle I_3 \rangle \quad (27)$$

and if, in the notation of § 3.1, we put $a_1 = G$, $a_2 = \lambda_1 S_1$, $a_3 = \lambda_2 S_2$, $a_4 = \lambda_3 S_3$ then

$$\langle I^2 \rangle = \langle S^4(1) \rangle.$$

For the space groups under consideration odd moments are zero, therefore

$$\begin{aligned} \langle I^2 \rangle &= \langle S(4) \rangle + 3 \langle S(2, 2) \rangle = \langle G^4 \rangle + \lambda_1^4 \langle S_1^4 \rangle \\ &+ \lambda_2^4 \langle S_2^4 \rangle + \lambda_3^4 \langle S_3^4 \rangle + 6 \langle G^2 \rangle \{ \lambda_1^2 \langle S_1^2 \rangle + \lambda_2^2 \langle S_2^2 \rangle \\ &+ \lambda_3^2 \langle S_3^2 \rangle \} + 6 \{ \lambda_1^2 \lambda_2^2 \langle S_1^2 \rangle \langle S_2^2 \rangle + \lambda_2^2 \lambda_3^2 \langle S_2^2 \rangle \langle S_3^2 \rangle \\ &+ \lambda_1^2 \lambda_3^2 \langle S_1^2 \rangle \langle S_3^2 \rangle \} \end{aligned}$$

or

$$\begin{aligned} \langle I^2 \rangle &= \langle I_g^2 \rangle + \sum_{r=1}^3 \lambda_r^4 \langle I_r^2 \rangle + 3 \sum_{r \neq s}^3 \sum_{r=1}^3 \lambda_r^2 \lambda_s^2 \langle I_r \rangle \langle I_s \rangle \\ &+ 6 \langle I_g \rangle \sum_{r=1}^3 \lambda_r^2 \langle I_r \rangle. \quad (28) \end{aligned}$$

Similarly

$$\langle I^3 \rangle = \langle S(6) \rangle + 15 \langle S(4, 2) \rangle + 15 \langle S(2, 2, 2) \rangle$$

giving

$$\begin{aligned} \langle I^3 \rangle &= \langle I_g^3 \rangle + \sum_{r=1}^3 \lambda_r^6 \langle I_r^3 \rangle + 15 \langle I_g^2 \rangle \sum_{r=1}^3 \lambda_r^2 \langle I_r \rangle \\ &+ 15 \langle I_g \rangle \sum_{r=1}^3 \lambda_r^4 \langle I_r^2 \rangle + 45 \langle I_g \rangle \sum_{r \neq s}^3 \sum_{r=1}^3 \lambda_r^2 \lambda_s^2 \langle I_r \rangle \langle I_s \rangle \\ &+ 15 \sum_{r \neq s}^3 \sum_{r=1}^3 \lambda_r^4 \lambda_s^2 \langle I_r^2 \rangle \langle I_s \rangle + 90 \lambda_1^2 \lambda_2^2 \lambda_3^2 \langle I_1 \rangle \langle I_2 \rangle \langle I_3 \rangle. \quad (29) \end{aligned}$$

4.2. *Non-centrosymmetrical space groups.* The most general expression can be written

$$F = G_R + \lambda_1 S_{1R} + \lambda_2 S_{2R} + \lambda_3 S_{3R} + j(G_I + \lambda_1 S_{1I} + \lambda_2 S_{2I} + \lambda_3 S_{3I}) \quad (30)$$

in which the contribution for the r th type of special position has been written as

$$F = \lambda_r (S_{rR} + j S_{rI}).$$

Following the notation of § 3.1, putting

$$\begin{aligned} a_1 &= G_R, \quad a_2 = \lambda_1 S_{1R}, \quad a_3 = \lambda_2 S_{2R}, \quad a_4 = \lambda_3 S_{3R} \\ b_1 &= G_I, \quad b_2 = \lambda_1 S_{1I}, \quad b_3 = \lambda_2 S_{2I}, \quad b_4 = \lambda_3 S_{3I}, \end{aligned}$$

we can write equation (30) as

$$F = S(1) + j S(1') \quad (31)$$

giving

$$\langle I \rangle = \langle S^2(1) + S^2(1') \rangle = \langle S(2) + S(2') \rangle$$

as only even powers are retained. Now

$$\langle I_g \rangle = \langle G_R^2 \rangle + \langle G_I^2 \rangle, \quad \langle I_1 \rangle = \langle S_{1R}^2 \rangle + \langle S_{1I}^2 \rangle$$

etc.; therefore

$$\langle I \rangle = \langle I_g \rangle + \lambda_1^2 \langle I_1 \rangle + \lambda_2^2 \langle I_2 \rangle + \lambda_3^2 \langle I_3 \rangle. \quad (32)$$

The second moment of intensity is

$$\langle I^2 \rangle = \langle S^4(1) + 2S^2(1)S^2(1') + S^4(1') \rangle$$

whence

$$\begin{aligned} \langle I^2 \rangle &= \langle S(4) \rangle + 3 \langle S(2, 2) \rangle + 3 \langle S(2', 2') \rangle \\ &+ 2 \langle S(22') \rangle + 2 \langle S(2, 2') \rangle + \langle S(4^2) \rangle. \quad (33) \end{aligned}$$

If we now notice that

$$\langle I_g^2 \rangle = \langle G_R^4 + 2G_R^2 G_I^2 + G_I^4 \rangle$$

and that for these space groups

$$\langle G_R^2 \rangle = \langle G_I^2 \rangle = \langle I_g \rangle / 2,$$

with similar results for I_1 , I_2 and I_3 , we deduce

$$\begin{aligned} \langle I^2 \rangle &= \langle I_g^2 \rangle + \sum_{r=1}^3 \lambda_r^4 \langle I_r^2 \rangle + 2 \sum_{r \neq s}^3 \sum_{r=1}^3 \lambda_r^2 \lambda_s^2 \langle I_r \rangle \langle I_s \rangle \\ &+ 4 \langle I_g \rangle \sum_{r=1}^3 \lambda_r^2 \langle I_r \rangle. \quad (34) \end{aligned}$$

Similarly,

$$\begin{aligned} \langle I^3 \rangle &= \langle I_g^3 \rangle + \sum_{r=1}^3 \lambda_r^6 \langle I_r^3 \rangle + 9 \langle I_g^2 \rangle \sum_{r=1}^3 \lambda_r^2 \langle I_r \rangle \\ &+ 9 \langle I_g \rangle \sum_{r=1}^3 \lambda_r^4 \langle I_r^2 \rangle + 18 \langle I_g \rangle \sum_{r \neq s}^3 \sum_{r=1}^3 \lambda_r^2 \lambda_s^2 \langle I_r \rangle \langle I_s \rangle \\ &+ 9 \sum_{r \neq s}^3 \sum_{r=1}^3 \lambda_r^4 \lambda_s^2 \langle I_r^2 \rangle \langle I_s \rangle + 36 \lambda_1^2 \lambda_2^2 \lambda_3^2 \langle I_1 \rangle \langle I_2 \rangle \langle I_3 \rangle. \quad (35) \end{aligned}$$

5. Hypersymmetry

It is possible in theory, though rarely in practice, to allow for the effects of hypersymmetry (Rogers & Wilson, 1953). As an example we shall consider the case of the asymmetric unit of *pmg* consisting of K parallel centrosymmetrical sub-units. The effective

asymmetric unit is now half one of the sub-units and contains $n/2K$ atoms, where n is the number of atoms in the asymmetric unit of the unit cell. Let x'_j, y'_j be the coordinates of the centre of symmetry of the j th sub-unit and let x_{ir}, y_{ir} be the coordinates of the i th atom in the j th effective asymmetric unit relative to the centre of symmetry of the j th sub-unit. The coordinates of the i th atom relative to the origin of the unit cell are therefore $x'_j + x_{ir}, y'_j + y_{ir}$. If we now replace $2\pi h x'_j, 2\pi k y'_j$ by α'_j, β'_j and $2\pi h x_{ir}, 2\pi k y_{ir}$ by θ_i, φ_i the structure factor expression is

$$F = \sum_{j=1}^K \cos \alpha'_j \cos \beta'_j \sum_{i=1}^{n/2K} f_i \cos \theta_i \cos \varphi_i + \sum_{j=1}^K \sin \alpha'_j \sin \beta'_j \sum_{i=1}^{n/2K} f_i \sin \theta_i \sin \varphi_i \quad (36)$$

which can be written as

$$F = A'A + B'B.$$

The α_j, β_j are independent of θ_i, φ_i ; therefore we have, on taking moments,

$$\begin{aligned} \langle I \rangle &= M'_{20} M_{20} + M'_{02} M_{02} \\ \langle I^2 \rangle &= M'_{40} M_{40} + 6M'_{22} M_{22} + M'_{04} M_{04} \\ \langle I^3 \rangle &= M'_{60} M_{60} + 15M'_{42} M_{42} + 15M'_{24} M_{24} + M'_{06} M_{06}, \end{aligned} \quad (37)$$

where

$$M_{rs} = \langle A^r B^s \rangle \text{ and } M'_{rs} = \langle A^{1r} B^{1s} \rangle.$$

Now because the expressions for A^1 and B^1 are of the same form as those for A and B we need only derive the partial moments M_{rs}, M'_{rs} being directly obtainable by putting f_i equal to unity in the expression for M_{rs} and assuming that there are K equal atoms. Any series $S^\beta(\alpha)$, therefore, in the expression for M_{rs} becomes K^β in the expression for M'_{rs} . The partial moments m_{rs} are

$$\begin{matrix} m_{20} & m_{02} & m_{22} & m_{40} & m_{04} & m_{42} & m_{24} & m_{60} & m_{06} \\ \frac{1}{4} & \frac{1}{4} & \frac{9}{64} & \frac{9}{64} & \frac{9}{64} & \frac{1}{256} & \frac{1}{256} & \frac{25}{256} & \frac{25}{256} \end{matrix}$$

and, using the expressions for M_{rs} given in Appendix 3, we have

$$\begin{aligned} M_{20} = M_{02} &= S(2)/4, & M'_{20} = M'_{02} &= K/4 \\ M_{22} &= S^2(2)/16 - 3S(4)/16, & M'_{22} &= K^2/16 - 3K/16 \\ M_{40} = M_{04} &= 3S^2(2)/16 - 3S(4)/16, \\ M'_{40} = M'_{04} &= 3K^2/16 - 3K/16 \end{aligned}$$

which give, by equation (37),

$$\begin{aligned} \langle I \rangle &= KS(2)/8 \\ \langle I^2 \rangle &= \frac{3}{64}(2K^2 - \frac{3}{4}K)S^2(2) - \frac{9}{256}(K^2 - \frac{1}{2}K)S(4). \end{aligned}$$

Similarly

$$\begin{aligned} \langle I^3 \rangle &= \frac{1}{512} \{ 90K^3 - \frac{495}{4}K^2 + \frac{75}{2}K \} S^3(2) \\ &\quad - \frac{1}{512} \{ \frac{495}{4}K^3 - 135K^2 + \frac{225}{4}K \} S(2)S(4) \\ &\quad + \frac{1}{512} \{ \frac{159}{4}K^3 - \frac{225}{4}K^2 + 25K \} S(6). \end{aligned}$$

APPENDIX I

A1-1. The series $S(\alpha_1, \alpha_2, \dots, \alpha_m)$ (§ 3.1) consists of terms of the type $a_{i_1}^{\alpha_1} a_{i_2}^{\alpha_2} \dots a_{i_m}^{\alpha_m}$ ($i_1 \neq i_2 \neq \dots \neq i_m$); from symmetry its value is invariant with respect to permutations of the indices α_i . Let $S_K(\alpha_1, \alpha_2, \dots, \alpha_m)$ represent the m -tuple series which does not contain a particular term a_K and let us assume that

$$S(\alpha_1, \alpha_2, \dots, \alpha_m) = \sum_{i=1}^m a_K^{\alpha_i} A_i(\alpha_1, \alpha_2, \dots, \alpha_{i-1}, \alpha_{i+1}, \dots, \alpha_m) + R, \quad (A1)$$

where A_i is a series whose terms do not have α_i as an index. On putting $a_K = 0$ we have $R = S_K(\alpha_1, \alpha_2, \dots, \alpha_m)$, and from the definition of $S(\alpha_1, \alpha_2, \dots, \alpha_m)$ (§ 3.1) the coefficient of $a_K^{\alpha_1}$ in (A1) is $S_K(\alpha_2, \alpha_3, \dots, \alpha_m)$. If α_i and α_1 are interchanged the series $S(\alpha_1, \alpha_2, \dots, \alpha_m)$ is unchanged, and therefore the coefficient of $a_K^{\alpha_1}$ is unchanged, giving

$$\begin{aligned} A_i(\alpha_i, \alpha_2, \dots, \alpha_{i-1}, \alpha_{i+1}, \dots, \alpha_m) \\ = S_K(\alpha_2, \alpha_3, \dots, \alpha_i, \dots, \alpha_m), \end{aligned}$$

from which

$$\begin{aligned} A_i(\alpha_1, \alpha_2, \dots, \alpha_{i-1}, \alpha_{i+1}, \dots, \alpha_m) \\ = S_K(\alpha_2, \alpha_3, \dots, \alpha_{i-1}, \alpha_1, \alpha_{i+1}, \dots, \alpha_m) \end{aligned}$$

giving, finally,

$$\begin{aligned} S(\alpha_1, \alpha_2, \dots, \alpha_m) \\ = \sum_{i=1}^m a_K^{\alpha_i} S_K(\alpha_1, \alpha_2, \dots, \alpha_{i-1}, \alpha_{i+1}, \dots, \alpha_m) \\ + S_K(\alpha_1, \alpha_2, \dots, \alpha_m). \end{aligned} \quad (A2)$$

Another result which follows immediately from the definitions of S and S_K is

$$\sum_{K=1}^n a_K^{\alpha_i} S_K(\alpha_1, \alpha_2, \dots, \alpha_{i-1}, \alpha_{i+1}, \dots, \alpha_m) = S(\alpha_1, \alpha_2, \dots, \alpha_m). \quad (A3)$$

A1-2. *Multiplication of series.* Consider the product $a_K^\beta S(\alpha_1, \alpha_2, \dots, \alpha_m)$. From equation (A2) we have

$$\begin{aligned} a_K^\beta S(\alpha_1, \alpha_2, \dots, \alpha_m) \\ = \sum_{i=1}^m a_K^{\alpha_i + \beta} S_K(\alpha_1, \alpha_2, \dots, \alpha_{i-1}, \alpha_{i+1}, \dots, \alpha_m) \\ + a_K^\beta S_K(\alpha_1, \alpha_2, \dots, \alpha_m). \end{aligned}$$

Therefore, on summing over K and using equation (A3),

$$\begin{aligned} S(\beta) \cdot S(\alpha_1, \alpha_2, \dots, \alpha_m) \\ = \sum_{i=1}^m S(\alpha_1, \alpha_2, \dots, \alpha_{i-1}, \alpha_i + \beta, \alpha_{i+1}, \dots, \alpha_m) \\ + S(\beta, \alpha_1, \alpha_2, \dots, \alpha_m). \end{aligned} \quad (A4)$$

Example

$$\begin{aligned} S(\theta) \cdot S(\alpha, \beta, \gamma) &= S(\theta + \alpha, \beta, \gamma) + S(\theta + \beta, \alpha, \gamma) \\ &\quad + S(\theta + \gamma, \alpha, \beta) + S(\alpha, \beta, \gamma, \theta). \end{aligned}$$

Consider the product $a_K^{\beta_1} S_K(\beta_2) \cdot S(\alpha_1, \alpha_2, \dots, \alpha_m)$ which, by equation (A2), can be written as

$$\sum_{i=1}^m a_K^{\beta_1 + \alpha_i} S_K(\beta_2) \cdot S_K(\alpha_1, \alpha_2, \dots, \alpha_{i-1}, \alpha_{i+1}, \dots, \alpha_m) + a_K^{\beta_1} S_K(\beta_2) S_K(\alpha_1, \alpha_2, \dots, \alpha_m).$$

On using equation (A4) we obtain

$$\sum_{i=1}^m a_K^{\beta_1 + \alpha_i} \times \left\{ \sum_{j \neq i}^m S_K(\alpha_1, \alpha_2, \dots, \alpha_j + \beta_2, \dots, \alpha_{i-1}, \alpha_{i+1}, \dots, \alpha_m) + S_K(\beta_2, \alpha_1, \alpha_2, \dots, \alpha_{i-1}, \alpha_{i+1}, \dots, \alpha_m) \right\} + a_K^{\beta_1} \sum_{i=1}^m S_K(\alpha_1, \alpha_2, \dots, \alpha_i + \beta_2, \dots, \alpha_m) + a_K^{\beta_1} S_K(\beta_2, \alpha_1, \alpha_2, \dots, \alpha_m)$$

and on summing over K we have, finally,

$$S(\beta_1, \beta_2) \cdot S(\alpha_1, \alpha_2, \dots, \alpha_m) = \sum_{i=1}^m \sum_{j \neq i}^m \times S(\alpha_1, \alpha_2, \dots, \alpha_j + \beta_2, \dots, \alpha_{i-1}, \alpha_i + \beta_1, \alpha_{i+1}, \dots, \alpha_m) + \sum_{i=1}^m \{ S(\beta_2, \alpha_1, \alpha_2, \dots, \alpha_{i-1}, \alpha_i + \beta_1, \alpha_{i+1}, \dots, \alpha_m) + S(\beta_1, \alpha_1, \alpha_2, \dots, \alpha_{i-1}, \alpha_i + \beta_2, \alpha_{i+1}, \dots, \alpha_m) \} + S(\alpha_1, \alpha_2, \dots, \alpha_m, \beta_1, \beta_2). \tag{A5}$$

There are four types of term in equation (A5); those in which β_1 and β_2 are added simultaneously to different α 's, those in which β_1 is added to an α_i and β_2 included as an extra index, those in which β_2 is added to an α_i and β_1 included as an extra index and those in which β_1 and β_2 are included as extra indices.

Examples

$$S(\alpha, \beta) \cdot S(\gamma, \delta) = S(\alpha + \gamma, \beta + \delta) + S(\alpha + \delta, \beta + \gamma) + S(\alpha + \delta, \beta, \gamma) + S(\alpha + \gamma, \beta, \delta) + S(\alpha, \beta + \gamma, \delta) + S(\alpha, \beta + \delta, \gamma) + S(\alpha, \beta, \gamma, \delta)$$

$$S(3, 1) \cdot S(2, 1, 1) = S(5, 1, 1, 1) + 2S(2, 4, 1, 1) + S(2, 3, 1, 1, 1) + S(3, 3, 1, 1) + 2S(3, 2, 2, 1) + 2S(5, 2, 1) + 2S(4, 3, 1) + 2S(4, 2, 2). \tag{A6}$$

The rules for multiplication by m -tuple series can be established by an induction procedure; they are similar to those for double series, $\beta_1, \beta_2, \dots, \beta_r$ being added simultaneously to different α 's, $\beta_1, \beta_2, \dots, \beta_{r-1}$ being added simultaneously to different α 's and β_r being included as an extra index and so on. For example, in the product $S^2(2, 1, 1)$ the additions in groups of three give $2S(4, 2, 2) + 4S(3, 3, 2)$; the factors 2 and 4 arise because 2, 1, 1 and 2, 1, 1 can be added to give 4, 2, 2 in two ways, the two 1's being considered distinct; similarly 2, 1, 1 and 2, 1, 1 can

be added to give 3, 3, 2 in four ways. On taking all groups into account we obtain, finally,

$$S^2(2, 1, 1) = 2S(4, 2, 2) + 4S(3, 3, 2) + 4S(4, 2, 1, 1) + 2S(2, 2, 2, 2) + 4S(3, 3, 1, 1) + 8S(3, 2, 2, 1) + 4S(2, 2, 2, 1, 1) + 4S(3, 2, 1, 1, 1) + S(4, 1, 1, 1, 1) + S(2, 2, 1, 1, 1, 1).$$

A1.3. The series $S(\beta^1)$ and $S(\alpha_1 \beta^1, \alpha_2, \dots, \alpha_m)$ were defined in § 3.1: to find the multiplication rule for products of the type $S(\beta^1) S(\alpha_1, \alpha_2, \dots, \alpha_m)$ we consider the term $b_K^\beta S(\alpha_1, \alpha_2, \dots, \alpha_m)$. From equation (A2) we have

$$b_K^\beta S(\alpha_1, \alpha_2, \dots, \alpha_m) = \sum_{i=1}^m a_K^{\alpha_i} b_K^\beta S_K(\alpha_1, \alpha_2, \dots, \alpha_{i-1}, \alpha_{i+1}, \dots, \alpha_m) + b_K^\beta S_K(\alpha_1, \alpha_2, \dots, \alpha_m)$$

and on summing over K we have

$$S(\beta^1) \cdot S(\alpha_1, \alpha_2, \dots, \alpha_m) = \sum_{i=1}^m S(\alpha_1, \alpha_2, \dots, \alpha_{i-1}, \alpha_i \beta^1, \alpha_{i+1}, \dots, \alpha_m) + S(\beta^1, \alpha_1, \alpha_2, \dots, \alpha_m). \tag{A7}$$

The multiplication rule in this case is formally the same as that in equation (A4), $\alpha_i \beta^1$ replacing $\alpha_i + \beta$, and it can be shown by the same method as before that the rules for multiplication by m -tuple series containing b_i 's are analogous to the previous ones; but, of course, the symbols must be interpreted according to the new definitions. Thus, by analogy with equation (A6),

$$S(\alpha, \beta) \cdot S(\gamma^1, \delta^1) = S(\alpha \gamma^1, \beta \delta^1) + S(\alpha \delta^1, \beta \gamma^1) + S(\alpha \delta^1, \beta, \gamma^1) + S(\alpha \gamma^1, \beta, \delta^1) + S(\alpha, \beta \gamma^1, \delta^1) + S(\alpha, \beta \delta^1, \gamma^1) + S(\alpha, \beta, \gamma^1, \delta^1). \tag{A8}$$

A1.4. From the relationship

$$S(\alpha_m) \cdot S(\alpha_1, \alpha_2, \dots, \alpha_{m-1}) = S(\alpha_1 + \alpha_m, \alpha_2, \dots, \alpha_{m-1}) + \dots + S(\alpha_1, \alpha_2, \dots, \alpha_m)$$

we have

$$S(\alpha_1, \alpha_2, \dots, \alpha_m) = S(\alpha_m) \cdot S(\alpha_1, \alpha_2, \dots, \alpha_{m-1}) - \text{series of order } (m-1). \tag{A9}$$

The series of order $(m-1)$ can similarly be reduced to series of order $(m-2)$, a process which can be continued until only products of single series remain. Any m -tuple series can therefore be expressed in terms of single series only.

Example

$$S(2, 1, 1) = S(2) \cdot S(1, 1) - 2S(3, 1) = S(2) \{ S^2(1) - S(2) \} - 2 \{ S(3) S(1) - S(4) \} = S^2(1) S(2) - S^2(2) - 2S(3) \cdot S(1) + 2S(4).$$

APPENDIX II

$$S^2(1) = S(2) + S(1, 1) \quad (\text{A10})$$

$$S^3(1) = S(3) + 3S(2, 1) + S(1, 1, 1) \quad (\text{A11})$$

$$S^4(1) = S(4) + 4S(3, 1) + 3S(2, 2) + 6S(2, 1, 1) + S(1, 1, 1, 1) \quad (\text{A12})$$

$$S^5(1) = S(5) + 5S(4, 1) + 10S(3, 2) + 10S(3, 1, 1) + 15S(2, 2, 1) + 10S(2, 1, 1, 1) + S(1, 1, 1, 1, 1) \quad (\text{A13})$$

$$S^6(1) = S(6) + 6S(5, 1) + 10S(3, 3) + 15S(2, 4) + 60S(3, 2, 1) + 20S(3, 1, 1, 1) + 15S(4, 1, 1) + 15S(2, 1, 1, 1, 1) + 45S(2, 2, 1, 1) + 15S(2, 2, 2) + S(1, 1, 1, 1, 1, 1) \quad (\text{A14})$$

$$S^7(1) = S(7) + 7S(6, 1) + 21S(5, 2) + 21S(5, 1, 1) + 35S(4, 3) + 70S(3, 3, 1) + 105S(4, 2, 1) + 105S(3, 2, 2) + 210S(3, 2, 1, 1) + 35S(4, 1, 1, 1) + 35S(3, 1, 1, 1, 1) + 105S(2, 2, 1, 1, 1) + 21S(2, 1, 1, 1, 1, 1) + 105S(2, 2, 2, 1) + S(1, 1, 1, 1, 1, 1, 1) \quad (\text{A15})$$

$$S^8(1) = S(8) + 8S(7, 1) + 28S(6, 2) + 28S(6, 1, 1) + 56S(5, 3) + 168S(5, 2, 1) + 56S(5, 1, 1, 1) + 35S(4, 4) + 280S(4, 3, 1) + 280S(3, 3, 2) + 280S(3, 3, 1, 1) + 210S(4, 2, 2) + 420S(4, 2, 1, 1) + 840S(3, 2, 2, 1) + 560S(3, 2, 1, 1, 1) + 70S(4, 1, 1, 1, 1) + 56S(3, 1, 1, 1, 1, 1) + 420S(2, 2, 2, 1, 1) + 210S(2, 2, 1, 1, 1, 1) + 28S(2, 1, 1, 1, 1, 1, 1) + 105S(2, 2, 2, 2) + S(1, 1, 1, 1, 1, 1, 1, 1) \quad (\text{A16})$$

APPENDIX III

Partial moments M_{pq}

$$M_{20} = m_{20}S(2)$$

$$M_{40} = 3m_{20}^2S^2(2) + \{m_{40} - 3m_{20}^2\}S(4)$$

$$M_{60} = 15m_{20}^3S^3(2) + \{15m_{20}m_{40} - 45m_{20}^3\}S(2) \cdot S(4) + 10m_{30}^2S^2(3) + \{30m_{20}^3 - 15m_{20}m_{40} - 10m_{30}^2 + m_{60}\}S(6)$$

$$M_{80} = 105m_{20}^4S^4(2) + \{28m_{20}m_{60} - 280m_{20}m_{30}^2 - 420m_{20}^2m_{40} + 840m_{20}^4\}S(2) \cdot S(6) + 280m_{20}m_{30}^2S(2)S^2(3) + \{210m_{20}^2m_{40} - 630m_{20}^4\}S^2(2)S(4) + \{315m_{20}^4 + 35m_{40}^2 - 210m_{20}^2m_{40}\}S^2(4) + \{56m_{30}m_{50} - 560m_{20}m_{30}^2\}S(3) \cdot S(5) + \{560m_{20}m_{30}^2 - 28m_{20}m_{60} + 420m_{20}^2m_{40} - 630m_{20}^4 - 56m_{30}m_{50} - 35m_{40}^2 + m_{80}\}S(8)$$

$$M_{22} = m_{20}m_{02}S^2(2) + \{m_{22} - m_{20}m_{02}\}S(4)$$

$$M_{24} = 3m_{20}m_{02}^2S^3(2) + \{m_{20}m_{04} - 9m_{20}m_{02}^2 + 6m_{22}m_{02}\}S(2) \cdot S(4) + 6m_{12}^2S^2(3) + \{6m_{20}m_{02}^2 - m_{20}m_{04} - 6m_{22}m_{02} + m_{24} - 6m_{12}^2\}S(6)$$

$$M_{42} = 3m_{20}^2m_{02}S^3(2) + \{m_{02}m_{40} - 9m_{02}m_{20}^2 + 6m_{22}m_{20}\}S(2)S(4) + 4m_{12}m_{30}S^2(3) + \{6m_{20}^2m_{02} - m_{02}m_{40} - 6m_{22}m_{20} + m_{42} - 4m_{12}m_{30}\}S(6)$$

$$M_{44} = 9m_{20}^2m_{02}^2S^4(2) + \{36m_{20}m_{02}m_{22} - 54m_{20}^2m_{02}^2 + 3m_{20}^2m_{04} + 3m_{02}^2m_{40}\}S^2(2) \cdot S(4) + \{27m_{20}^2m_{02}^2 - 3m_{20}^2m_{04} - 36m_{20}m_{02}m_{22} - 3m_{02}^2m_{40} + 18m_{22}^2 + m_{40}m_{04}\}S^2(4) + \{6m_{20}m_{24} - 72m_{20}m_{02}m_{22} + 72m_{20}^2m_{02}^2 - 6m_{20}^2m_{04} - 36m_{20}^2m_{12}^2 - 6m_{02}^2m_{40} + 6m_{02}m_{42} - 24m_{02}m_{12}m_{30}\} \times S(2) \cdot S(6) + \{36m_{20}m_{12}^2 + 24m_{02}m_{12}m_{30}\}S(2) \cdot S^2(3) + \{4m_{30}m_{14} + 24m_{32}m_{12} - 72m_{20}m_{12}^2 - 48m_{02}m_{12}m_{30}\}S(3) \cdot S(5) + \{72m_{20}m_{12}^2 + 72m_{20}m_{02}m_{22} - 6m_{20}m_{24} - 54m_{20}^2m_{02}^2 + 6m_{20}^2m_{04} - 6m_{02}m_{42} + 48m_{02}m_{12}m_{30} + 6m_{02}^2m_{40} + m_{44} - m_{04}m_{40} - 18m_{22}^2 - 24m_{12}m_{32} - 4m_{14}m_{30}\}S(8)$$

$$M_{62} = 15m_{20}^3m_{02}S^4(2) + \{15m_{20}m_{02}m_{40} + 45m_{20}^2m_{22} - 90m_{20}^3m_{02}\}S^2(2) \cdot S(4) + \{45m_{20}^3m_{02} - 15m_{20}m_{40}m_{02} - 45m_{20}^2m_{22} + 15m_{22}m_{40}\}S^2(4) + \{15m_{20}m_{42} - 30m_{20}m_{02}m_{40} - 60m_{20}m_{30}m_{12} - 90m_{20}^2m_{22} + 120m_{20}^3m_{02} + m_{60}m_{02} - 10m_{30}^2m_{02}\}S(2) \cdot S(6) + \{60m_{20}m_{30}m_{12} + 10m_{30}^2m_{02}\}S(2) \cdot S^2(3) + \{20m_{30}m_{32} - 120m_{20}m_{30}m_{12} - 20m_{30}^2m_{02} + 6m_{50}m_{12}\}S(3) \cdot S(5) + \{30m_{20}m_{02}m_{40} + 120m_{20}m_{12}m_{30} - 15m_{20}m_{42} + 90m_{20}^2m_{22} - 90m_{20}^3m_{02} - 15m_{22}m_{40} + m_{62} + 20m_{30}^2m_{02} - 20m_{30}m_{32} - 6m_{50}m_{12} - m_{60}m_{02}\}S(8)$$

$$M_{26} = 15m_{20}m_{02}^3S^4(2) + \{15m_{20}m_{02}m_{04} + 45m_{22}m_{02}^2 - 90m_{20}m_{02}^3\}S^2(2) \cdot S(4) + \{45m_{20}m_{02}^3 - 15m_{20}m_{02}m_{04} - 45m_{22}m_{02}^2 + 15m_{22}m_{04}\}S^2(4) + \{m_{20}m_{06} + 120m_{20}m_{02}^3 - 30m_{20}m_{02}m_{04} - 90m_{22}m_{02}^2 + 15m_{02}m_{24} - 90m_{02}m_{12}^2\}S(2) \cdot S(6) + 90m_{02}m_{12}^2S(2) \cdot S(3) + \{30m_{12}m_{14} - 180m_{02}m_{12}^2\}S(3) \cdot S(5) + \{30m_{20}m_{04}m_{02} - 90m_{20}m_{02}^3 - m_{20}m_{06} + 90m_{22}m_{02}^2 - 15m_{24}m_{02} + m_{26} - 15m_{22}m_{04} - 30m_{12}m_{14} + 180m_{02}m_{12}^2\}S(8)$$

APPENDIX IV

The geometrical structure factor of the plane group $p6$ is

$$A = \cos 2\pi(hx + ky) + \cos 2\pi\{kx - (h+k)y\} + \cos 2\pi\{hy - (h+k)x\}. \quad (\text{A17})$$

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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References

- COLLIN, R. L. (1955). *Acta Cryst.* **8**, 499.
 FOSTER, F. & HARGREAVES, A. (1963). *Acta Cryst.* **16**, 1133.
 HARGREAVES, A. (1955). *Acta Cryst.* **8**, 12.
 HARGREAVES, A. (1956). *Acta Cryst.* **9**, 191.
 HAUPTMAN, H. & KARLE, J. (1953). *Acta Cryst.* **6**, 136.
 HERBSTSTEIN, F. H. & SCHOENING, F. R. L. (1957). *Acta Cryst.* **10**, 657.
 HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
International Tables for X-ray Crystallography (1959). Vol. II, p. 355. Birmingham: Kynoch.
 KARLE, J. & HAUPTMAN, H. (1953). *Acta Cryst.* **6**, 131.
 KLUG, A. (1958). *Acta Cryst.* **11**, 515.
 LIPSON, H. & WOOLFSON, M. M. (1952). *Acta Cryst.* **5**, 680.
 ROGERS, D. & WILSON, A. J. C. (1953). *Acta Cryst.* **6**, 439.
 SIM, G. A. (1958a). *Acta Cryst.* **11**, 123.
 SIM, G. A. (1958b). *Acta Cryst.* **11**, 420.
 WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318.
 WILSON, A. J. C. (1951). *Research*, **4**, 141.
 WILSON, A. J. C. (1956). *Acta Cryst.* **9**, 143.

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