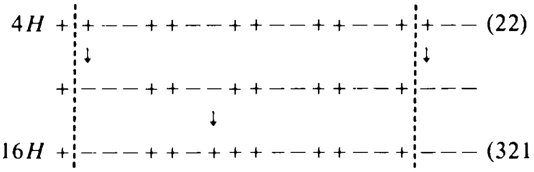
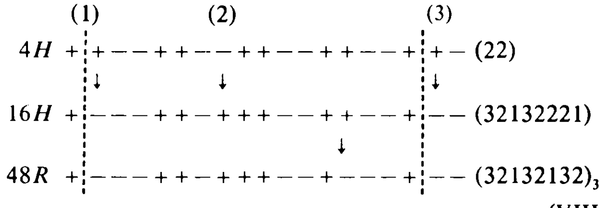
de type $4H$ dans laquelle est favorisée l'extension d'une deuxième faute distante de $6d_S$ de la première conduisant alors à $12H$.

(d) $n = 4$ ($P = 16$)



(VII)

Comme pour $n = 3$, l'extension d'une seule faute, ainsi répétée toutes les 16 couches de soufre, conduit à une structure possédant une longue séquence de type $4H$; d'autres fautes doivent donc s'y développer. Si une deuxième faute, distante de la première de $6d_S$ se développe, on obtient le polytype $16H$ (3213221) dont la structure correspond bien à celle qui a été déterminée expérimentalement. Il subsiste malgré tout dans ce cas une zone relativement étendue de structure (22) non fautée dans laquelle sera favorisée l'extension d'une faute distante de $6d_S$ de celles existant déjà dans le cristal. Deux possibilités sont alors offertes: développement de la faute à une distance $6d_S$ de la faute notée (2), ou bien de la faute notée (3). Ces deux éventualités conduisent toutes deux au même résultat: $48R$ [soit $(32132131)_3$, soit $(32131321)_3$ qui ne différent que par une permutation circulaire].



(VIII)

On peut noter que l'extension de cette troisième famille de fautes doit être moins favorisée que celle des premières en raison du fait qu'elle se trouve à une distance inférieure à $6d_S$ d'une autre faute.

De façon générale, on constate que l'apparition des polytypes déjà observés s'explique par l'existence des dislocations vis les plus probables dans $4H$: celles qui ont les vecteurs de Burgers les plus courts. Les plus fréquemment observés ($12R$, $8H$, $24R$) correspondent aux dislocations vis les plus fréquentes ($V_B = 4$ et $8d_S$) alors que $12H$, $16H$ et $48R$, issus de dislocations de vecteurs de Burgers plus longs (12 et $16d_S$), sont plus rares.

La coïncidence qu'on peut remarquer entre les résultats expérimentaux disponibles (période, structure et fréquence d'apparition des polytypes) et les effets qu'on peut attendre du mécanisme proposé confirme la validité de ce dernier. Ainsi les polytypes de sulfure de titane peuvent être considérés comme le résultat de transformations de phase dans un milieu cristallin imparfait.

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Variance of X-ray Intensities: Effect of Dispersion and Higher Symmetries

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The variance of X-ray intensities is $W = \Sigma^2 + (k-1)S^2 - \sum_i Q_i|f_i|^4$, where Σ is the sum of the squares of the moduli of the atomic scattering factors f_i, S is the modulus of the sum of the squares of the atomic scattering factors, k is 1 for noncentrosymmetric crystals and 2 for centrosymmetric, Q_i is an integer depending on the space group and Wyckoff position, and the summation is over the atoms of the asymmetric unit. Values of Q_i for the general reflexions and general positions are tabulated for the line, plane and space groups; they tend to be moderately positive for the less symmetric space groups and large and negative for the more symmetric. Special reflexions and special positions are discussed briefly. Dispersion shows itself in the distinction between Σ and S and in the modulus signs in the final term.

1. Introduction

1.1. Wilson (1951) derived expressions for the variance of the intensity of X-ray reflexions from crystals belonging to the space groups $P1$ and $P\bar{1}$. The subject has become of some interest again in connexion with the values of the residual R_2 [Wilson, 1969, 1974, 1976; Lenstra, 1974, and private communications; see Srinivasan & Parthasarathy (1976) for numerous references]. It is also relevant to statistical tests for the determination of space groups. Those proposed by Wilson (1949*a*,*b*, 1950*a*,*b*, 1951), Howells, Phillips & Rogers (1949, 1950) and others [for references see Srinivasan & Parthasarathy (1976)] either make the assumption that the intensity distribution function has one of the ideal asymptotic forms (Wilson, 1949*b*) or that interactions between symmetry elements are negligible. As will be seen below, in some noncentrosymmetric space groups of high symmetry there are interactive effects that shift their statistical properties some way toward those of centrosymmetric space groups otherwise of low symmetry.

1.2. The variance of the intensity of X-ray reflexions having roughly the same values of $(\sin\theta)/\lambda$ is defined by

$$W = \langle |F|^4 \rangle - \langle |F|^2 \rangle^2, \qquad (1)$$

where F is the structure factor of the *hkl* reflexion and the averaging is over values of *hkl*. It is well known that

$$\langle |F|^2 \rangle = \sum_i |f_i|^2 \qquad (2)$$

$$= \Sigma, \qquad (3)$$

where Σ is the sum of the squares of the moduli of the scattering factors of the atoms in one unit cell of the crystal (Wilson, 1942). If the averaging is done over zones or rows of reflexions, instead of over the whole array, the average intensity may be greater than Σ (Wilson, 1950*a*,*b*), a phenomenon that may aid space-group determination (Rogers, 1950). The increased intensity of such a zone or row is compensated by a decrease in the neighbouring region of reciprocal space (Wilson, 1964). For the present purpose it is convenient to group together atoms equivalent by symmetry (atoms occupying the same 'Wyckoff position'). Equation (2) then becomes

$$\langle |F|^2 \rangle = \sum_i p_i |f_i|^2, \qquad (4)$$

where p_i is the multiplicity (number of symmetry-equivalent atoms) of the Wyckoff position and the summation is now over all non-equivalent groups of atoms.

1.3. There are no such simple general results for the average values of the fourth power of the modulus of the structure factor. The problem was considered by Karle & Hauptmann (1953) and Hauptmann & Karle (1953) in connexion with structure determination for the space groups $P1$ and $P\bar{1}$ already treated by Wilson (1951), and for some other space groups in later papers. Wilson (1976), generalizing results obtained by Foster & Hargreaves (1963), quoted without proof the equation

$$\langle |F|^4 \rangle = 2\Sigma^2 + (k-1)S^2 - \sum_i [(1+k)p_i^2 - q_i] |f_i|^4, \qquad (5)$$

where S is the modulus of the sum of the squares of the atomic scattering factors (and is thus different from Σ, the sum of the squares of the moduli of the atomic scattering factors, when dispersion is appreciable), k is 1 for noncentrosymmetric crystals and 2 for centrosymmetric, and q_i is a number depending on the space

Table 1. *Some statistical properties of line and plane groups (one- and two-dimensional space groups)*

All entries refer to general Wyckoff positions. Except as indicated in the column headed 'Special reflexions', the values of p_i, q_i and Q_i refer to general (*hk*) reflexions.

Group	p_1	q_1	Q_i	Special reflexions	p_i	q_i	Q_i
$\mathscr{p}1$	1	1	1	None			
$\mathscr{p}m$	2	6	6	None			
*p*1	1	1	1	None			
*p*2	2	6	6	None			
pm	2	6	2	0*k*	4	16	16
				*h*0	2	6	6
pg	2	6	2	0*k*, *k* even	4	16	16
				odd	0	0	0
				average	2	8	8
				*h*0	2	6	6
cm				*hk*, *h* + *k* even	8	96	32
				odd	0	0	0
				average	4	48	16
				0*k*, *k* even	16	256	256
				odd	0	0	0
				average	8	128	128
				*h*0, *h* even	8	96	96
				odd	0	0	0
				average	4	48	48
pmm	4	36	12	*h* or *k* = 0	8	96	96
pmg	4	36	12	0*k*	8	96	96
				*h*0, *h* even	8	96	96
				odd	0	0	0
				average	4	48	48
pgg	4	36	12	0*k*, *k* *h*0, *h* } even	8	96	96
				odd	0	0	0
				average	4	48	48
cmm				*hk*, *h* + *k* even	16	576	192
				odd	0	0	0
				average	8	288	96
				0*k*, *k* *h*0, *h* } even	32	1536	1536
				odd	0	0	0
				average	16	768	768
*p*4	4	36	12	None			
*p*4*m*	8	168	24	0*k* or *h*0	16	288	480
*p*4*g*	8	168	24	0*k*, *k* *h*0, *h* } even	16	288	480
				odd	0	0	0
				average	8	144	240
*p*3	3	15	3	None			
*p*3*m*1	6	66	6	*h* = *k etc.*	6	90	18
				h etc. = 0	12	240	48
*p*31*m*	6	66	6	*h* = −*k etc.*	6	90	18
				h etc. = 0	12	240	48
*p*6	6	90	18	None			
*p*6*m*	12	396	36	*hh* or 0*k* or *h*0	24	1440	288

group and the Wyckoff position. It is, in fact, the mean value of the fourth power of the trigonometrical structure factor for the Wyckoff position, and is shown to be an integer in § 3.2. The summation is over all non-equivalent groups of atoms; not all groups need occupy the same Wyckoff position. It is convenient to introduce a symbol for the multiplier of $|f_i|^4$:

$$Q_i = (1+k)p_i^2 - q_i. \tag{6}$$

Foster & Hargreaves pointed out that the space groups in the triclinic, monoclinic and orthorhombic systems can be arranged in seven categories that have the same values of p_i, q_i and Q_i for the general reflexions, within trivial factors depending on the lattice, but the two space groups $Fdd2$ and $Fddd$ are exceptions. These exceptions are in accordance with a general empirical rule (§ 3.4): the statistical properties of the general reflexions depend only on the point group if the space group contains no single symmetry element of multiplicity higher than three.

1.4. The present paper gives the derivation of equation (5) and evaluates q_i and Q_i for the general reflexions and general Wyckoff positions for the remaining space groups. The values for the line groups (one-dimensional space groups) and plane groups (two-dimensional space groups) are given in Table 1. These groups are simple enough for the table to contain some

Table 2. *Some statistical properties of the three-dimensional space groups with primitive lattices*

All entries refer to general Wyckoff positions, and (except where indicated in the final column) to general (*hkl*) reflexions.

Point group	Space group(s)	p_i	q_1	Q_i	Notes
1	$P1$	1	1	1	
$\bar{1}$	$P\bar{1}$	2	6	6	
2	All P	2	6	2	See Table 7
m	All P	2	6	2	See Table 7
$2/m$	All P	4	36	12	See Table 7
222	All P	4	28	4	
$mm2$	All P	4	36	−4	
mmm	All P	8	216	−24	
4	$P4$, $P4_2$	4	36	−4	
	$P4_1$, $P4_3$	4	36	−4	l even
		4	20	12	l odd
		4	28	4	average
$\bar{4}$	$P\bar{4}$	4	28	4	
$4/m$	All P	8	216	−24	
422	$P422$, $P42_12$, $P4_222$, $P4_22_12$	8	136	−8	
	$P4_122$, $P4_322$, $P4_12_12$, $P4_32_12$	8	136	−8	l even
		8	104	24	l odd
		8	120	8	average
$4mm$	All P	8	168	−40	
$\bar{4}2m$	All P	8	136	−8	
$\bar{4}m2$	All P	8	136	−8	
$4/mmm$	All P	16	1008	−240	
3	All P and R	3	15	3	
$\bar{3}$	Both	6	90	18	
32	All P and R	6	66	6	
$3m$	All P and R	6	66	6	
$\bar{3}m$	All P and R	12	396	36	
6	$P6$, $P6_3$	6	90	−18	
	$P6_1$, $P6_2$, $P6_4$, $P6_5$	6	90	−18	$l = 3n$
		6	54	18	$l \neq 3n$
		6	66	6	average
$\bar{6}$	$P\bar{6}$	6	90	−18	
$6/m$	$P6/m$, $P6_3/m$	12	540	−108	
622	$P622$, $P6_322$	12	324	−36	
	$P6_122$, $P6_222$, $P6_422$, $P6_522$	12	324	−36	$l = 3n$
		12	252	36	$l \neq 3n$
		12	276	12	average
$6mm$	All P	12	396	−108	
$\bar{6}m2$	All P	12	396	−108	
$6/mmm$	All P	24	2376	−648	
23	Both P	12	276	12	
$m3$	All P	24	1800	−72	
432	$P432$, $P4_232$	24	1272	−120	
	$P4_132$, $P4_332$	24	1272	−120	any index even
		24	984	144	all indices odd
		24	1200	−48	average
$\bar{4}3m$	Both P	24	1272	−120	
$m3m$	All P	48	8784	−1872	

Table 3. *Some statistical properties of the three-dimensional space groups with body-centred lattices*

All entries refer to general Wyckoff positions and general (*hkl*) reflexions.

Point group	Space group(s)	p_i	q_i	Q_i
222	$I222$, $I2_12_12_1$	8	224	32
$mm2$	$Imm2$, $Iba2$, $Ima2$	8	288	−32
mmm	$Immm$, $Ibam$, $Ibca$, $Imma$	16	1728	−192
4	$I4$	8	288	−32
	$I4_1$	8	224	32
$\bar{4}$	$I\bar{4}$	8	224	32
$4/m$	$I4/m$	16	1728	−192
	$I4_1/a$	16	1536	0
422	$I422$	16	1088	−64
	$I4_122$	16	960	64
$4mm$	$I4mm$, $I4cm$	16	1344	−320
	$I4_1md$, $I4_1cd$	16	1088	−64
$\bar{4}2m$	$I\bar{4}m2$, $I\bar{4}c2$, $I\bar{4}2m$	16	1088	−64
	$I\bar{4}2d$	16	960	64
$4/mmm$	$I4/mmm$, $I4/mcm$	32	8064	−1920
	$I4_1/amd$, $I4_1/acd$	32	6528	−384
23	$I23$, $I2_13$	24	2208	96
$m3$	$Im3$, $Ia3$	48	14400	−576
432	$I432$, $I4_132$	48	10176	−960
$\bar{4}3m$	$I\bar{4}3m$, $I\bar{4}3d$	48	10176	−960
$m3m$	$Im3m$, $Ia3d$	96	70272	−14976

Table 4. *Some statistical properties of the three-dimensional space groups with end-centred (one-face-centred) lattices*

All entries refer to general Wyckoff positions and general (*hkl*) reflexions.

Point group	Space group(s)	p_i	q_i	Q_i
2	$B2$	4	48	16
m	Bm, Bb	4	48	16
$2/m$	$B2/m$, $B2/b$	8	288	96
$mm2$	$Cmm2$, $Cmc2_1$, Ccc, $Amm2$, $Abm2$, $Ama2$, $Aba2$	8	288	−32
mmm	$Cmcm$, $Cmca$, $Cmmm$, $Cccm$, $Cmma$, $Ccca$	16	1728	−192

information about zones and rows of reflexions as well. Values for three-dimensional space groups with primitive lattices are given in Table 2, with end-centred lattices in Table 3, with body-centred lattices in Table 4, and with face-centred lattices in Table 5. The calculations of q_i from the trigonometrical structure factors become very tedious and subject to human error for the more symmetric space groups, and some upper bounds for Q_i and lower bounds for q_i are given in Table 6. The derivation of these bounds is given in § 3.5, and their use has led to the detection of several errors in the calculation. It is observed empirically that q_i and Q_i are integral multiples of p_i; all apparent exceptions were found on recalculation to be incorrect. This observation suggests that there should be some more direct method of evaluating Q_i, but none has been found. Special sets of reflexions and special Wyckoff positions are briefly discussed in §§ 5 and 6.

1.5 For a given number of atoms in the Wyckoff position, the trend is for the variance to increase with increasing symmetry, though 'degree of symmetry' is perhaps to some extent subjective. The variance is, from equations (1), (5) and (6),

$$W = \langle |F|^4 \rangle - \langle |F|^2 \rangle^2 \tag{7}$$

$$= \Sigma^2 + (k-1)S^2 - \sum_i Q_i |f_i|^4. \tag{8}$$

Addition of a centre of symmetry to whatever symmetry may already have been present thus approximately doubles the variance for the same cell content. The effect of other symmetry elements is generally small in comparison. The first term in equation (8) and the middle term for centrosymmetric crystals are approximately proportional to the square of the number of atoms in the unit cell, whereas the third term, the only one that depends on symmetry other than centrosymmetry, is roughly proportional to the first power of the number of atoms. Its effect is thus proportionally small when the total number of atoms is large but the values of p_i are small or moderate. It could become comparable with the other terms if the total number of atoms is only moderate, but the crystal is highly symmetric, so that p_i is large and Q_i is large and negative. To illustrate this, imagine an accommodating element that crystallizes in three allotropic forms, each with 24 atoms in the unit cell. The triclinic form, space group $P1$, has

$$W = 1(24)^2 f^4 - 24 f^4$$

$$= 552 f^4. \tag{9}$$

The monoclinic form, space group $P2/m$, with six atoms in the asymmetric unit, has

$$W = 2(24)^2 f^4 - 6(12 f^4)$$

$$= 1080 f^4, \tag{10}$$

while the hexagonal form, space group $P6/mmm$, with one atom in the asymmetric unit, has

$$W = 2(24)^2 f^4 + 648 f^4$$

$$= 1800 f^4. \tag{11}$$

(Dispersion has been neglected; the values of Q_i needed are taken from Table 2.) In this extreme case, therefore, going from moderate to high symmetry has a greater effect than going from no symmetry to moderate centrosymmetry.

Table 5. *Some statistical properties of the three-dimensional space groups with face-centred lattices*

All entries refer to general Wyckoff positions and general (*hkl*) reflexions.

Point group	Space group(s)	p_i	q_i	Q_i
222	*F*222	16	1792	256
*mm*2	*Fmm*2	16	2304	−256
	*Fdd*2	16	1792	256
mmm	*Fmmm*	32	13824	−1536
	Fddd	32	10752	1536
23	*F*23	48	17664	768
*m*3	*Fm*3	96	115200	−4608
	*Fd*3	96	105984	4608
432	*F*432	96	81408	−7680
	$F4_132$	96	72192	768
$\bar{4}3m$	$F\bar{4}3m$, $F\bar{4}3c$	96	81408	−7680
*m*3*m*	*Fm*3*m*, *Fm*3*c*	192	562176	−119808
	*Fd*3*m*, *Fd*3*c*	192	?	?

Table 6. *Lower bounds for q_i and upper bounds for Q_i for some symmetry elements and combinations of symmetry elements*

Minimum symmetry	Minimum q_i	Maximum Q_i
1	$2p_i^2 - p_i$	p_i
$\bar{1}$	$3p_i^2 - 3p_i$	$3p_i$
$\bar{4}$	$2p_i^2 + p_i$	$-p_i$
$4 + \bar{1}$ (4/*m*)	$3p_i^2 + 3p_i$	$-3p_i$
$\bar{6}$	$2p_i^2 + 3p_i$	$-3p_i$
$6 + \bar{1}$ (6/*m*)	$3p_i^2 + 9p_i$	$-9p_i$

1.6. It should perhaps be mentioned explicitly that the variance of X-ray intensities under discussion here is that inherent in the atomic arrangement. The variance actually observed will be increased by statistical fluctuations in the counting rates and other experimental difficulties (Wilson, 1951), and would be decreased by uncorrected extinction (Rogers, Stanley & Wilson, 1955). The variance would also be altered by any non-crystallographic symmetry (Lipson & Woolfson, 1952; Wilson, 1952, 1956; Rogers & Wilson, 1953). In practical applications it is often advantageous to normalize the structure factors in the sense of Bertaut (1955), as larger ranges of $(\sin\theta)/\lambda$ can be used in the averaging.

1.7. The numerical values in the tables have been checked in various ways, and numerous errors in the initial calculations have been corrected. It cannot be hoped, however, that the tables are entirely free from error, especially for the more symmetric space groups with large numbers of atoms in the Wyckoff position. Though the tables give a correct overall impression, it is recommended that any value required for a specific application should be recalculated independently. The author would be glad to receive notification of any errors found.

2. Calculation of the mean-square intensity

2.1. The expressions for structure factors are all of the form

$$F = \sum_i f_i J_i, \tag{12}$$

where f_i is the scattering factor of the atom in the ith Wyckoff position and J_i is a trigonometrical expression depending on the atomic coordinates x_i, y_i, z_i and the indices of reflexion h,k,l. The f's and J's may be purely real, or complex, depending on the space group and the importance of dispersion. The J's are listed in *International Tables for X-ray Crystallography* (1952) for the general Wyckoff positions. They have the property that when averaged over a large set of values of hkl

$$\langle J_i J_i^* \rangle = p_i \tag{13}$$

with variance $q_i - p_i^2$,

$$\langle J_i J_j^* \rangle = 0, \quad i \neq j, \tag{14}$$

with variance p_i^2, where, as in equation (4), p_i is the multiplicity of the ith Wyckoff position and q_i has the same significance as in equation (5). For the noncentrosymmetric space groups there are two further relations:

$$\langle J_i J_i \rangle = 0 \tag{15}$$

with variance q_i, and

$$\langle J_i J_j \rangle = 0 \tag{16}$$

with variance p_i^2. The intensity of a reflexion is, from equation (12),

$$I = FF^* = \sum_{ij} f_i f_j^* J_i J_j^*, \tag{17}$$

so that the average intensity of a reflexion is

$$\langle I \rangle = \sum_i p_i f_i f_i^* = \sum_i p_i |f_i|^2, \tag{18}$$

recovering equation (4). The square of the intensity of a reflexion is given by the square of equation (17):

$$I^2 = \sum_{ijkl} f_i f_j^* f_k f_l^* J_i J_j^* J_k J_l^*. \tag{19}$$

In view of equations (14)–(16) most terms in the expression for I^2 vanish on averaging over a large set of values of hkl; those that remain have i, j, k, l equal in pairs. For noncentrosymmetric structures those that survive have either $i = j$ and $k = l$ or $i = l$ and $j = k$, so that

$$(1) \qquad \langle I^2 \rangle = 2 \sum_{i \neq k} |f_i|^2 |f_k|^2 \langle |J_i|^2 \rangle \langle |J_k|^2 \rangle + \sum_i |f_i|^4 \langle |J_i|^4 \rangle \tag{20}$$

$$= 2 \sum_{i \neq k} p_i p_k |f_i|^2 |f_k|^2 + \sum_i q_i |f_i|^4, \tag{21}$$

in view of equation (13) and the definition of q_i. The double sum in equation (21) is almost separable into two factors, and becomes so if the terms with $i = k$ are supplied. To preserve the equality these terms must be subtracted again, so that

$$(1) \qquad \langle I^2 \rangle = 2 \left(\sum_i p_i |f_i|^2 \right)^2 - \sum_i (2p_i^2 - q_i) |f_i|^4, \tag{22}$$

in agreement with equation (5) with $k = 1$.

2.2. For centrosymmetric structures $J_i^* = J_i$, though f_i^* is only equal to f_i in the absence of dispersion. There are thus more terms surviving when I^2 is averaged over a large set of values of hkl: those with $i = j$, $k = l$; those with $i = k, j = l$; and those with $i = l$, $j = k$. Thus

$$(\bar{1}) \qquad \langle I^2 \rangle = \sum_{i \neq k} p_i p_k |f_i|^2 |f_k|^2 + \sum_{i \neq l} p_i p_l f_i^2 (f_i^*)^2 + \sum_{i \neq j} p_i p_j |f_i|^2 |f_j|^2 + \sum_i q_i |f_i|^4. \tag{23}$$

Once again the double sums are almost separable into two factors, and become so if the terms with $i = k$ *etc.* are supplied. On adding and subtracting these terms, to preserve the equality, equation (23) becomes

$$(\bar{1}) \quad \langle I^2 \rangle = 2 \left(\sum_i p_i |f_i|^2 \right)^2 + \left(\sum_i p_i f_i^2 \right) \left[\sum_j p_j (f_j^*)^2 \right] - \sum_i (3p_i^2 - q_i) |f_i|^4. \tag{24}$$

On using equation (4) for Σ and the modulus of

$$\mathbf{S} = \sum_i p_i f_i^2 \tag{25}$$

for S, equation (5) with $k = 2$ follows.

2.3. The mean value of $|J_i|^4$ can be obtained straightforwardly, though often tediously, from the expressions for J given in *International Tables*. For example, for the space group $Pmm2$ and an atom in the general position,

$$J = 4(\cos 2\pi hx \cos 2\pi ky \cos 2\pi lz + i \cos 2\pi hx \cos 2\pi ky \sin 2\pi lz), \tag{26}$$

$$|J|^2 = 16 \cos^2 2\pi hx \cos^2 2\pi ky \, (\cos^2 2\pi lz + \sin^2 2\pi lz) = 16 \cos^2 2\pi hx \cos^2 2\pi ky, \tag{27}$$

$$|J|^4 = 256 \cos^4 2\pi hx \cos^4 2\pi ky. \qquad (28)$$

On averaging over a large set of values of h the mean value of $\cos^4 2\pi hx$ is $\frac{3}{8}$, and similarly for the factor in ky. For this space group and this position, therefore,

$$q = \langle |J|^4 \rangle = 36, \qquad (29)$$

$$Q = 2p^2 - q = -4. \qquad (30)$$

With slightly more complication the same result is obtained for the general reflexions and the general positions for $Pmc2_1$, $Pcc2$, $Pma2$, $Pca2_1$, $Pnc2$, $Pmn2_1$, $Pba2$, $Pna2_1$ and $Pnn2$, the other space groups with primitive lattices in the point group $mm2$. The end- and body-centred space groups of this point group differ only through trivial factors (§ 4.1), but for $Fdd2$ half the reflexions have quite a different form for $|J|^4$, and hence essentially different values of q and Q. For special sets of reflexions even the space groups with primitive lattices may give other values of q and Q.

3. Patterson interpretation of mean-square intensity

3.1. It is well known that the Patterson synthesis (Patterson, 1935) can be regarded as a pseudo-structure consisting of pseudo-atoms of 'atomic' scattering factor $f_i^* f_j$ situated at positions corresponding to the vector joining the atoms i and j of the real structure, and that the 'structure factors' of the pseudo-structure are equal to the intensities of the real structure [for an elementary discussion see, for example, Wilson (1970, pp. 177–178)]. The 'intensities' given by the pseudo-structure are thus equal to the squares of the intensities of the real structure, and their mean value is thus what is required in the evaluation of the variance of the intensities of the real structure. By analogy with the result

$$\langle I \rangle = \langle |F|^2 \rangle = \sum_i |f_i|^2 \qquad (31)$$

for the real structure, one obtains

$$\langle I^2 \rangle = \langle (|F|^2)^2 \rangle = \sum_{ij} |f_i^* f_j|^2 \qquad (32)$$

$$= \sum_{ij} |f_i|^2 |f_j|^2 \qquad (33)$$

for the pseudo-structure, allowances being made in equation (31) for coincidences of atoms (Wilson, 1942) and in equation (33) for coincidences of Patterson pseudo-atoms. In the case of the real structure coincidences do not occur for general hkl reflexions, but may do so for zones such as $hk0$ or rows such as $00l$ (Wilson, 1950*a*,*b*). For the Patterson pseudo-structure, however, all self vectors ($i = j$) are bound to coincide at the origin, whatever the space group, and there may be other coincidences for general reflexions in many space groups, and coincidences for zones and rows in many more space groups.

3.2. For the calculation of p_i and q_i one need only consider point atoms occupying one Wyckoff position. The mean intensity is thus p_i for the general reflexions, but possibly higher for zones and rows; coincidences increasing p_i are immediately deducible from Tables 1 and 2 of Wilson (1950*b*) or Table 3 of Rogers (1950). The mean (intensity)² will be q_i. There are necessarily p_i point pseudo-atoms coinciding at the origin of the Patterson pseudo-structure. If there are no other coincidences there will be a further $p_i(p_i - 1)$ point pseudo-atoms, so that

$$q_i = (p_i)^2 + p_i(p_i - 1) \qquad (34)$$

$$= 2p_i^2 - p_i. \qquad (35)$$

The corresponding values of Q_i are

$$\text{(noncentrosymmetric)} \quad Q_i = 2p_i^2 - q_i = p_i, \qquad (36)$$

$$\text{(centrosymmetric)} \quad Q_i = 3p_i^2 - q_i = p_i^2 + p_i. \qquad (37)$$

Whether or not there are further coincidences, the Patterson approach expresses q_i as a sum of integers, and thus q_i and Q_i are necessarily integers – a deduction by no means obvious from the interpretation of q_i as the mean value of the fourth power of the modulus of the trigonometric structure factor.

3.3. It is clear that there cannot be further vector coincidences if p_i is three or less – the minimum possibility for a multiple non-origin peak arises for a Wyckoff position with four points at the corners of a parallelogram – so that the values of q_i and Q_i given by equations (35)–(37) will be correct for all space groups with primitive lattices in the point groups 1, $\bar{1}$, 2, m and 3. For other space groups these equations set minimum values for q_i and maximum values for Q_i.

3.4. The point groups with general Wyckoff positions of multiplicity four are $2/m$, 222, $mm2$, 4 and $\bar{4}$. In 222 and $\bar{4}$ the points do not form a parallelogram, and equations (35) and (36) apply. In $P2/m$, $Pmm2$ and $P4$ the points form an obvious rectangle or square, so that the Patterson map consists of a fourfold coincidence at the origin, four vectors of single weight (the diagonals of the rectangle or square, counted in both directions), and four vectors of double weight (the parallel sides of the rectangle or square, counted in both directions). The mean-square Patterson 'intensity' is thus

$$q_i = 4(1)^2 + 4(2)^2 + 4^2 = 36, \qquad (38)$$

so that

$$Q_i = 2(4)^2 - 36 = -4 \qquad (39)$$

in the noncentrosymmetric space groups ($Pmm2$, as already derived by the structure-factor method in § 2.3, and *P*4), and

$$Q_i = 3(4)^2 - 36 = 12 \tag{40}$$

in the centrosymmetric space group *P*2/*m*. The other space groups with primitive lattices in the point groups 2/*m* and *mm*2 also have Wyckoff positions in the form of a parallelogram (not necessarily right-angled), so the same values of q_i and Q_i apply. (For some space groups one of the points conventionally tabulated must be ignored, and replaced by an equivalent point in an adjoining unit cell, before the parallelogram is obvious.)

There are three other space groups with primitive lattices in the point group 4: $P4_1$, $P4_2$, and $P4_3$. Of these, $P4_2$ exhibits a parallelogram inclined to the fourfold axis (not perpendicular to it, as in *P*4), and so has the same values of q_i and Q_i as *P*4, but $P4_1$ and $P4_3$ do not form parallelograms, and for them q_i and Q_i revert to those of equations (35) and (36). The difference in behaviour of the primitive space groups in the point groups *mm*2 and 4 illustrates the empirical rule, mentioned in § 1.3, that the values of q_i and Q_i depend only on the point group for the general reflexions if there is no single symmetry element present with multiplicity higher than three, whereas they may depend on the space group if there is a single symmetry element with multiplicity four or more. The formation, or otherwise, of parallelograms, polygons or prisms with parallel edges goes some way toward giving it a theoretical foundation. A further property of $P4_1$ and $P4_3$ may be mentioned in passing: for the present purposes their statistical behaviour is the same as that of *P*4 when *l* is even, but like that of *P*2 with two independent groups of two atoms when *l* is odd. Other space groups with fourfold or sixfold screw axes behave analogously; the significance, or otherwise, of this behaviour has not been pursued.

3.5. Use of equations (35) and (36) with inequality signs inserted,

$$q_i \geq 2p_i^2 - p_i, \tag{41}$$

$$(1) \qquad Q_i \leq p_i, \tag{42}$$

led to the discovery of several errors in the trial calculations of $\langle |J_i|^4 \rangle$ for noncentrosymmetric space groups. For centrosymmetric space groups equation (41) is not very limiting, and the equivalent of equation (42),

$$(\bar{1}) \qquad Q_i \leq p_i^2 + p_i, \tag{43}$$

obtained by inserting the inequality sign in equation (37), is almost useless. More informative equations can be obtained in the following way. For space groups other than $P\bar{1}$, a centre of symmetry forces the vector between the points of the Wyckoff position to be parallel in pairs, except for the vectors between points actually related by the centre of symmetry. This is a special case of the property noted by Patterson (1949): a centrosymmetric group of atoms is forced by an external crystallographic centre of symmetry to be parallel to its centrosymmetrically related counterpart. In the present application the 'centrosymmetric group' consists only of two Wyckoff points. The Patterson map of the Wyckoff position thus consists of p_i self vectors coinciding at the origin, p_i vectors of single weight joining points related by the centre of symmetry, and $\frac{1}{2}p_i(p_i - 2)$ vectors of double weight. Since any further coincidences would increase q_i,

$$(\bar{1}) \qquad q_i \geq (p_i)^2 + p_i(1)^2 + \tfrac{1}{2}p_i(p_i - 2)(2)^2 = 3p_i^2 - 3p_i, \tag{44}$$

and

$$(\bar{1}) \qquad Q_i \leq 3p_i. \tag{45}$$

These equations led similarly to the discovery of numerical errors in the trial calculations for centrosymmetric space groups. Similar Patterson calculations can be made for other symmetry elements and combinations of them; a few are collected in Table 6. They all give lower bounds for q_i and upper bounds for Q_i, and there is no obvious way of fixing the corresponding upper and lower bounds. For some space groups q_i is very large and positive, Q_i large and negative (2376 and −648 for *P*6/*mmm*, 8784 and −1872 for *Pm*3*m*). Some guidance concerning coincidences leading to such large values can be obtained from Table 1 of Buerger (1950), but I have not been able to formulate a method of deducing necessary and sufficient conditions from it.

4. Effect of centring

4.1. Some space groups with centred lattices (such as *Cmm*2, *Imm*2, *Fmm*2; *Cmmm*, *Fmmm*, *Immm*) differ from the corresponding space groups with primitive lattices (*Pmm*2; *Pmmm*) only in that the multiplicity of the Wyckoff position is doubled or quadrupled by the translations implicit in the lattice. For such space groups p_i is multiplied by two for body- or end-centred lattices and by four for face-centred lattices; the reflexions actually present are enhanced by a factor of 2^2 or 4^2, but only one-half or one-quarter of the reflexions have non-zero intensity. Similarly the values of q_i are increased by factors of $8 = \frac{1}{2}(2)^4$ and $64 = \frac{1}{4}(4)^4$ respectively. The values of p_i, q_i and Q_i are only trivially different from those of the primitive space groups in such cases. For other space groups (Foster & Hargreaves noted *Fdd*2 and *Fddd*; other examples are $I4_1/a$, and $I4_1md$) there is no corresponding primitive space group, and p_i, q_i and Q_i have to be calculated independently.

4.2. Values of p_i, q_i and Q_i for space groups with body-, end-, and face-centring are given in Tables 3, 4 and 5 respectively. For ease of reference those that differ only trivially from the corresponding space groups with primitive lattices are included, as well as those that depend essentially on the lattice centring.

5. Zones and rows of reflexions

5.1. Certain zones or rows of reflexions in space groups of symmetry higher than $P\bar{1}$ differ in their statistical properties from those of the general reflexions. These special reflexions, in the context of this paper, correspond to those of a two-dimensional crystal produced by projecting the real crystal along an axis on to a plane, or along a plane on to an axis. In a sense, therefore, there is nothing to be said about them that is not implicit in Table 1, which gives the properties of the line and plane groups. The plane groups corresponding to the special reflexions are given in *International Tables* for each space group.

5.2. There are two features that make special reflexions of interest in the present context. First, a projection can be centrosymmetric even when the space group is not, thus changing k in equation (5) and later equations from 1 to 2. (The converse cannot occur.) For example, the special reflexions with h or k or l zero for the space group $P2_12_12_1$ have p_i unchanged at 4, but q_i increases from 28 to 36 and Q_i from 4 to 12, the values for the plane group *pgg*.

The second feature is that atoms that are distinct in space may coincide in projection. The easiest of these coincidences to visualize is that of a mirror plane; a pair of atoms of atomic scattering factor f at x,y,z; $x,y,\bar{z}$ becomes a single 'atom' of atomic scattering factor $2f$ in the projection along c on to the plane, and must be so counted in calculating the statistical properties of the $hk0$ reflexions (Wilson, 1942, 1950*a*,*b*). Thus the values 4, 36, 12 for p_i, q_i, Q_i for the hkl reflexions in the space group $P2/m$ become 8, 96, 96 for the $hk0$ reflexions. These correspond to the values for the plane group $p2$ scaled up by the factor 2^2 or 2^4, as appropriate.

Table 7. *Some statistical properties of special reflexions for the monoclinic space groups with primitive lattices and general Wyckoff positions, setting c unique*

Space	$hk0$			$00l$			
group	p_i	q_i	Q_i	p_i	q_i	Q_i	Notes
$P2$	2	6	6	4	16	16	
$P2_1$	2	6	6	4	16	16	l even
				0	0	0	l odd
				2	8	8	average
Pm	4	16	16	2	6	6	
Pb	4	16	16	2	6	6	k even
	0	0	0				k odd
	2	8	8				average
$P2/m$	8	96	96	8	96	96	
$P2_1/m$	8	96	96	8	96	96	l even
				0	0	0	l odd
				4	48	48	average
$P2/b$	8	96	96	8	96	96	k even
	0	0	0				k odd
	4	48	48				average
$P2_1/b$	8	96	96	8	96	96	k, l even
	0	0	0	0	0	0	k, l odd
	4	48	48	4	48	48	average

5.3. Scaling up the plane-group values, or working from the Patterson-map approach, needs very clear thinking about weighting of the multiple 'atoms' and the corresponding vectors. In view of possible complications, if the statistical properties of special reflexions are required it is probably best to calculate them *ab initio* from the structure-factor expressions in *International Tables*. A change in k is indicated by the vanishing of the imaginary part of the structure factor (or, in some space groups where the choice of origin has not been made with this application in view, by the vanishing of the real and the imaginary parts alternately). The calculations of q_i are somewhat less tedious than for the general reflexions, but it has not been thought worth while to tabulate them in detail. For the sake of illustration, those for the plane groups are given in Table 1, and those for the primitive monoclinic space groups in Table 7.

6. Special positions

6.1. The current *International Tables* give no help in the calculations of p_i, q_i and Q_i for atoms in the special Wyckoff positions, since the points of a special position do not necessarily conform to a symmetry group, though anything occupying one of them must have the symmetry of a point group. Their arrangement has whatever symmetry is left after the symmetry of this point group has been removed from the symmetry of the space group. 'Special positions always have as point symmetry a point group. Removing the operations of this point group from the space group means to remove the operations of a complete symmorphic space group which is a subgroup of the space group in question. What remains are the cosets of this subgroup with respect to the non-removed space-group operations. The latter class includes all glides and screws and those point-group operations which are not part of the point symmetry of the special position. These cosets do not form a group and are to be considered as just a set of operations' (Hahn, 1977). For some of the more symmetric space groups the considerations of Fischer (1971, 1973; Koch, 1974) are relevant.

6.2. It seems, therefore, that it is necessary to obtain the values of q_i directly from the coordinates of the special position, either by first writing the expression for the trigonometric structure factor and proceeding as in § 2.3, or by constructing the Patterson map, as in § 3. Any special position involves, of course, less work than does the general position of the same space group, but some space groups have many special positions (*P6/mmm*, for example, has 17, and *Pm3m* has 13). It has not been thought worth while to undertake the task without a practical end in view.

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X-ray Scattering Factors for O^{2-} and N^{3-}

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Form factors calculated from several theoretical models show that the $X\alpha$ method is accurate to about 1%. With the latter scheme and the Watson-sphere model the atomic form factors for O^{2-} and N^{3-} are computed for varying sphere radii. To a first approximation this radial variation accounts for the different environments of such ions. Deviations of up to 25% in the scattering factors occur when compared with the results obtained from the wave functions of the corresponding neutral atom.

1. Introduction

Coherent X-ray scattering factors are available for atoms (see, for example, Fraga, Karwowski & Saxena, 1976) and some positive and negative ions (Cromer & Mann, 1968). However, free negative ions such as O^{2-} or N^{3-} are unstable and therefore the corresponding form factors are not easily obtainable. For an investigation of Li_3N (Schulz & Schwarz, 1978) we were interested in studying the effects of an ionic crystal on the form factors of ions, especially on negative ions which are otherwise unstable.

Although free O^{2-} ions are not observed experimentally, crystalline O^{2-} ions are stabilized by their