

indices of 200 and 020 respectively to the middle of three intense spots which appear on the second festoon of zero-level b - and a -axis Weissenberg photographs. Constants for such a cell appear in Table 3. The fact that the tilt of this c axis from the normal to the ab

soaps, 18.4; β acid soaps, 19.0; A potassium caprate, 18.5 \AA^2 .

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Table 3. Constants for physical unit cell, $\epsilon \text{RSO}_3\text{Na} \cdot \frac{1}{2}\text{H}_2\text{O}$

Substance	a_0 (A.)	b_0 (A.)	c_0 (A.)	α	β	γ	τ_c^*
$\text{C}_{12}\text{H}_{25}\text{SO}_3\text{Na} \cdot \frac{1}{2}\text{H}_2\text{O}$	9.90	10.76	40.63	113° 14'	110° 29'	111° 6'	41° 46'
$\text{C}_{14}\text{H}_{29}\text{SO}_3\text{Na} \cdot \frac{1}{2}\text{H}_2\text{O}$	9.92	10.76	45.87	113° 37'	110° 29'	110° 28'	41° 17'
$\text{C}_{16}\text{H}_{33}\text{SO}_3\text{Na} \cdot \frac{1}{2}\text{H}_2\text{O}$	9.92	10.77	50.57	114° 27'	108° 46'	111° 32'	41° 0'
$\text{C}_{18}\text{H}_{37}\text{SO}_3\text{Na} \cdot \frac{1}{2}\text{H}_2\text{O}$	9.93	10.82	56.05	114° 38'	108° 59'	111° 23'	41° 25'

* Tilt of c axis from normal to ab plane.

Calculation of tilt from Δd_{001} and Δ theoretical chain-length change: average $\tau = 41^\circ 27'$.

plane is the same as the tilt of the chains calculated from Δd_{001} indicates that the chains probably lie along the c axis.

Using the angle of tilt as $41\frac{1}{2}^\circ$, we may calculate the effective cross-section of the molecules normal to the chain axis, $\sigma = \frac{1}{2}a_0b_0 \sin \gamma \cos \tau$. Thus we obtain 18.6 \AA^2 . This value may be compared with those obtained for some other substances: α sodium 1-alkanesulfonates, 20–21; β sodium 1-alkanesulfonates, 18.1; γ sodium 1-alkanesulfonates, 23.0; δ sodium 1-alkanesulfonates, 22.4; $\text{C}_n\text{H}_{2n+2}$, 18.2; α sodium soaps, 18.2; α acid

of Washington which made it possible for one of us (L.H.J.) to work on the later stages of the problem.

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The Probability Distribution of X-ray Intensities. III. Effects of Symmetry Elements on Zones and Rows

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A symmetry element that causes equivalent atoms to coincide in groups of n in a plane (or line) projection produces a zone (or row) of reflexions whose average intensity is $n\Sigma$, where Σ is the sum of the squares of the scattering factors of the atoms in the unit cell. The average for the general reflexions is Σ ; the difference between the zone (or row) average and the general average may be useful in the purely X-ray determination of space groups. The effects of simple symmetry elements on the probability distribution of the intensities are summarized in two tables.

1. Introduction

The first statistical treatment of the intensity of X-ray reflexions showed that the average intensity of the general (hkl) reflexions is given by

$$\langle I \rangle = \sum_{j=1}^N f_j^2 \equiv \Sigma, \quad (1)$$

where f_j is the scattering factor of the j th atom and the sum is over all atoms in the cell (Wilson, 1942; Harker, 1948; Hughes, 1949). More refined consideration, based on the central limit theorem, showed that the probability of the hkl reflexion from a non-centrosymmetric

crystal having an intensity I is given by the acentric* (A) distribution function

$${}_1P(I) = S^{-1} \exp\{-I/S\}, \quad (2)$$

where S is a distribution parameter, and by the centric* (C) distribution function

$${}_2P(I) = (2\pi SI)^{-\frac{1}{2}} \exp\{-I/2S\}, \quad (3)$$

if the crystal is centrosymmetric (Wilson, 1949). The centric distribution was discovered empirically by Hughes (1949), and both distributions have been verified

* These convenient adjectives were suggested by Rogers (1949).

experimentally by Howells, Phillips & Rogers (1950). These functions are valid not only for the general reflexions (hkl), but also for those corresponding to plane projections (say $hk0$) and line projections (say $00l$).

For the *general* reflexions from a crystal referred to a primitive lattice the distribution parameter S has the value Σ . In a centred crystal it has the value 4Σ

Table 1. *Intensity-distribution effects of symmetry elements not causing systematic absences*

A =acentric distribution, C =centric distribution, S =distribution parameter, $\langle I \rangle$ =average intensity. Axes are parallel to \mathbf{c} , planes perpendicular to \mathbf{c} .

Element	Reflexions	Distribution	$S/\Sigma = \langle I \rangle / \Sigma$
1	All	A	1
$\bar{1}$	All	C	1
2	hkl	A	1
	$hk0$	C	1
	$00l$	A	2
$\bar{2} \equiv m$	hkl	A	1
	$hk0$	A	2
	$00l$	C	1
3	hkl	A	1
	$hk0$	A	1
	$00l$	A	3
$\bar{3}$	hkl	C	1
	$hk0$	C	1
	$00l$	C	3
4	hkl	A	1
	$hk0$	C	1
	$00l$	A	4
$\bar{4}$	hkl	A	1
	$hk0$	C	1
	$00l$	C	2
6	hkl	A	1
	$hk0$	C	1
	$00l$	A	6
$\bar{6} \equiv 3/m$	hkl	A	1
	$hk0$	A	2
	$00l$	C	3

(face-centring) or 2Σ (end- or body-centring) for the reflexions that actually appear (Wilson, 1949), though the average intensity $\langle I \rangle$ remains equal to Σ . For *zones* and *rows* of reflexions, however, both $\langle I \rangle$ and S may be two or more times as great as Σ . The reason for this has been pointed out by Wilson (1942), and in a restricted sense by Hughes (1949); if two or more atoms coincide in projection, they simulate a single atom with scattering factor equal to the sum of their individual scattering factors. As the scattering factors are squared in the expression for $\langle I \rangle$, the effect is to increase its value. If the space group is such that equivalent atoms coincide in groups of n , the average intensity becomes

$$\langle I \rangle = \sum_{j=1}^{N/n} (nf_j)^2 = n\Sigma, \quad (4)$$

and, if there are no systematic absences in the zone or row corresponding to the projection, the distribution parameter S has the same value.

In the present paper the effects of simple symmetry elements on the intensity distribution in zones and rows

are derived. The notation is that of Wilson (1949). Only the mirror plane is treated in detail; once the general principle has been grasped, the effects can be written down without calculation. For convenience of reference they are collected in Tables 1 and 2, which include also results already published. Planes of symmetry are taken perpendicular to \mathbf{c} , the axes of symmetry parallel to \mathbf{c} . Their use in space-group determination will be discussed by Dr D. Rogers in a later paper in this series.

Table 2. *Intensity-distribution effects of symmetry elements causing systematic absences*

A =acentric distribution, C =centric distribution, Z =systematically zero, S =distribution parameter, $\langle I \rangle$ =average intensity. Axes are parallel to \mathbf{c} , planes perpendicular to \mathbf{c} .

Element	Reflexions	Distribution	$\langle I \rangle / \Sigma$	S/Σ
2_1	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$\frac{1}{2}Z + \frac{1}{2}A$	1	2
$3_1, 3_2$	hkl	A	1	1
	$hk0$	A	1	1
	$00l$	$\frac{2}{3}Z + \frac{1}{3}A$	1	3
$4_1, 4_3$	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$\frac{3}{4}Z + \frac{1}{4}A$	1	4
4_2	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$\frac{1}{2}Z + \frac{1}{2}A$	2	4
$6_1, 6_5$	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$\frac{5}{6}Z + \frac{1}{6}A$	1	6
$6_2, 6_4$	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$\frac{2}{3}Z + \frac{1}{3}A$	2	6
6_3	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$\frac{1}{2}Z + \frac{1}{2}A$	3	6
a	hkl	A	1	1
	$hk0$	$\frac{1}{2}Z + \frac{1}{2}A$	1	2
	$00l$	C	1	1
	$0k0$	A	2	2
C	All	$\frac{1}{2}Z + \frac{1}{2}A$	1	2
I	All	$\frac{1}{2}Z + \frac{1}{2}A$	1	2
F	All	$\frac{3}{4}Z + \frac{1}{4}A$	1	4

2. Symmetry elements without systematic absences

2.1. Mirror plane

In a crystal containing a mirror plane equivalent atoms occur in pairs with co-ordinates $(u, v, \pm w)$. The structure amplitude is therefore

$$\begin{aligned} F &= \sum_{j=1}^{\frac{1}{2}N} f_j [\exp\{2\pi i(hu_j + kv_j + lw_j)\} \\ &\quad + \exp\{2\pi i(hu_j + kv_j - lw_j)\}] \\ &= 2 \sum_{j=1}^{\frac{1}{2}N} f_j \cos 2\pi(hu_j + kv_j) \cos 2\pi lw_j \\ &\quad + 2i \sum_{j=1}^{\frac{1}{2}N} f_j \sin 2\pi(hu_j + kv_j) \cos 2\pi lw_j, \end{aligned} \quad (5)$$

and the random variables are

$$\left. \begin{aligned} \xi_j &= 2f_j \cos 2\pi(hu_j + kv_j) \cos 2\pi lw_j, \\ \eta_j &= 2f_j \sin 2\pi(hu_j + kv_j) \cos 2\pi lw_j. \end{aligned} \right\} \quad (6)$$

Except for a few low-order reflexions the average value of each of these is zero, so that the mean-square deviations are

$$\alpha_j^2 = 4f_j^2 \langle \cos^2 2\pi(hu_j + kv_j) \rangle \langle \cos^2 2\pi lw_j \rangle$$

$$= f_j^2 \quad (l \neq 0, \quad h \text{ and } k \neq 0), \quad (7)$$

$$= 2f_j^2 \quad (l=0 \text{ or } h \text{ and } k=0), \quad (8)$$

$$\beta_j^2 = 4f_j^2 \langle \sin^2 2\pi(hu_j + kv_j) \rangle \langle \cos^2 2\pi lw_j \rangle$$

$$= f_j^2 \quad (l \neq 0, \quad h \text{ and } k \neq 0), \quad (9)$$

$$= 2f_j^2 \quad (l=0), \quad (10)$$

$$= 0 \quad (h \text{ and } k=0). \quad (11)$$

The parameters A and B in the distribution function

$$P(x, y) dx dy = (2\pi AB)^{-1} \exp\{-x^2/2A^2 - y^2/2B^2\} dx dy \quad (12)$$

(Wilson, 1949, equation 19, with $X=0$) are given by

$$A^2 = \sum_{j=1}^{\frac{1}{2}N} \alpha_j^2 = \frac{1}{2}\Sigma \quad (l \neq 0, \quad h \text{ and } k \neq 0), \quad (13)$$

$$= \Sigma \quad (l=0 \text{ or } h \text{ and } k=0), \quad (14)$$

$$B^2 = \sum_{j=1}^{\frac{1}{2}N} \beta_j^2 = \frac{1}{2}\Sigma \quad (l \neq 0, \quad h \text{ and } k \neq 0), \quad (15)$$

$$= \Sigma \quad (l=0), \quad (16)$$

$$= 0 \quad (h \text{ and } k=0). \quad (17)$$

For the general (hkl) reflexions these give

$$P(x, y) dx dy = (\pi\Sigma)^{-1} \exp\{-(x^2 + y^2)/\Sigma\} dx dy, \quad (18)$$

which reduces to the acentric distribution (2) with $S = \Sigma$ on putting $x^2 + y^2 = I$. For the $hk0$ zone, however, $S = 2\Sigma$, though the distribution function is still acentric. For the $00l$ row $B=0$ and equation (12) is indeterminate, but on taking the limit as $B \rightarrow 0$ it becomes the centric distribution (3) with $S = \Sigma$. The average intensity, equal to $A^2 + B^2$ (Wilson, 1949, equation 20), is equal to Σ for the hkl and $00l$ reflexions, but for the $hk0$ reflexions it is 2Σ .

These results are exactly those that would be expected from the observations (i) that equivalent atoms coincide in pairs in the projection on the mirror plane, (ii) that the projection on a line perpendicular to the mirror plane is centrosymmetric. The remaining simple symmetry elements may therefore be treated very briefly, the number of equivalent atoms coinciding and the centrosymmetry or otherwise of a projection being a sufficient guide to the type and parameter of the distribution functions.

2.2. Rotation axes

When n is even, the n -fold rotation axes give a centrosymmetric plane projection, and hence a centric distribution of $hk0$ intensities. In the projection on to the axes, equivalent atoms coincide in groups of n , so that S and $\langle I \rangle$ are equal to $n\Sigma$ for the $00l$ reflexions.

2.3. Inversion axes

The twofold inversion axis is the same as a mirror plane. The threefold axis implies a centre of symmetry,

so that all intensity distributions are centric. In the projection on to the axis equivalent atoms coincide in groups of three, making S and $\langle I \rangle$ equal to 3Σ . The fourfold axis gives a centrosymmetric plane projection; in the projection on to the axis pairs of atoms coincide, giving S and $\langle I \rangle$ equal to 2Σ . The sixfold axis is equivalent to a threefold rotation axis with a perpendicular mirror plane, thus giving $S = \langle I \rangle = 2\Sigma$ for the $hk0$ reflexions and a centrosymmetric line projection with $S = \langle I \rangle = 3\Sigma$. (The progression of $\langle I \rangle = \Sigma, 2\Sigma, 3\Sigma$ for the $hkl, hk0$ and $00l$ reflexions is rather interesting, and it is unfortunate that there is no certain example of the class $\bar{6}$ to investigate.)

3. Symmetry elements involving systematic absences

3.1. Distinction between $\langle I \rangle$ and S

The chief peculiarity introduced by symmetry elements involving absences is that the average intensity is no longer necessarily equal to the distribution parameter. This has already been discussed for centring (Wilson, 1949), and can be avoided formally by referring the reflexions to the primitive cell or, for projections on to glide planes or screw axes, the apparent primitive cell. Expressed otherwise, the average intensity of the reflexions that appear is equal to the distribution parameter for the reflexions that appear, but the average of all reflexions is reduced by those of zero intensity.

3.2. Screw axes

When n is even, the n_m screw axes give a centrosymmetric plane projection, and hence a centric distribution of $hk0$ intensities. When n and m have a common factor p , equivalent atoms coincide in groups of p in the projection on to the axis, thus raising $\langle I \rangle$ to $p\Sigma$. The m/n or $(n-m)/n$ systematic absences further increase S to $n\Sigma$.

3.3. Glide planes

An a glide makes half the intensities zero in the $hk0$ projection, so that for these reflexions S is 2Σ , and gives a centrosymmetric projection on to c , so that the $00l$ reflexions have a centric distribution. In the projection on to b , equivalent atoms coincide in pairs, so that the $0k0$ reflexions have $\langle I \rangle$ and S equal to 2Σ .

Irreducible d glides occur only in connexion with other symmetry elements, and may perhaps best be considered with the determination of space groups.

4. Discussion

The numerical differences in $\langle I \rangle$ described here are considerably greater than those in the ratio $\rho \equiv \langle F \rangle^2 / \langle I \rangle$ (Wilson, 1949), or in the integral distribution functions ${}_1N(z)$ and ${}_2N(z)$ (Howells *et al.* 1950). They should be particularly useful when discrimination between space groups depends on a row of reflexions only, so that the number of reflexions is too small for a satisfactory

determination of the integral distribution function. Further, the differences in $\langle I \rangle$ depend on less subtle principles than do the differences between the distribution functions, and are less likely to be upset by deviations from the ideal of a random distribution of a large number of atoms of approximately the same scattering factor. Heavy atoms in general positions should not be troublesome, though those in special positions may cause anomalies.

The writer's thanks are due to Dr D. Rogers, whose unpublished work on Patterson syntheses showed

qualitatively that effects of the type discussed here must exist and should be sought.

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The Crystal Structure of Mo₃Si

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The crystal structure of Mo₃Si has been determined from powder-diffraction patterns. The lattice is cubic with $a = 4.890 \pm 0.002$ Å. The structure is that of β -wolfram and the compound is isostructural with Cr₃Si and V₃Si.

An investigation of the phase diagram of the molybdenum-silicon system has been made in this laboratory by Searcy (1949) and L. Brewer, who heated known mixtures of the elements and submitted them to us for X-ray examination. A new phase was found whose composition corresponded to MoSi_{0.35 ± 0.05}. Powder-diffraction patterns of this phase were obtained using copper $K\alpha$ X-rays with a 9 cm. diameter powder camera and with a 'Norelco' spectrometer. The density of a small sample was determined by measurement of its apparent weights in air and in toluene. From these data it was possible to deduce the complete structure by a straightforward procedure depending only on the reflections of zero intensity. The result was checked by computation of the intensities of the observed lines.

The diffraction patterns corresponded to a primitive cubic lattice with

$$a = 4.890 \pm 0.002 \text{ Å.}$$

The density measured by buoyancy was 8.4 ± 0.3 g.cm.⁻³, where the uncertainty is due to the weighing error of the small sample used. This value corresponds to a molecular weight of 592. The composition MoSi_{0.35 ± 0.05} deduced from the phase studies corresponds to 91 ± 1 % molybdenum. Thus there are 5.6 ± 0.3 , i.e. 6 molybdenum atoms, and 2.1 ± 0.3 , or 2 silicon atoms in each unit cell. For Mo₆Si₂ the density calculated from the X-ray measurement is 8.97 ± 0.01 g.cm.⁻³. The difference from the measured value is not regarded as significant, because of the porous appearance of the sample tested by buoyancy.

Reflections were observed for planes hhl only if

$l = 2n$. Also absent were 410, 430 and 531. All other lines up to $h^2 + k^2 + l^2 = 38$ were observed. These extinctions limit the space group to $O_h^3 - Pm\bar{3}n$ and $T_d^4 - P\bar{4}3n$, which have sets of 2, 6, 8, 12 and more equivalent positions. The twofold and sixfold special positions for these two space groups are identical, so it is sufficient to consider O_h^3 . The two silicon atoms must be in 2(a): 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Molybdenum in 6(b): 0, $\frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$; 0, 0, $\frac{1}{2}$; 0, $\frac{1}{2}, 0$; $\frac{1}{2}, 0, 0$ does not permit the observed reflections 210, 320, 421, and others. The two remaining sets 6(c) and 6(d) differ by the translation $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, and therefore give equivalent structures when combined with 2(a). Such a combination moreover requires all the observed extinctions. Therefore, the structure is:

Space group $O_h^3 - Pm\bar{3}n$.

2 Si in (a): 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

6 Mo in (c): $\frac{1}{4}, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{4}, 0$; 0, $\frac{1}{2}, \frac{1}{4}$; $\frac{3}{4}, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{3}{4}, 0$; 0, $\frac{1}{2}, \frac{1}{4}$.

Intensities were calculated for this structure by the equation

$$I = p |F_{hkl}|^2 \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \times 3.3 \times 10^{-5},$$

where F_{hkl} is the structure factor, p is the multiplicity, and θ is the Bragg angle. The numerical factor reduces the intensities to the arbitrary scale of the spectrometer values. The agreement of these intensities with the observed values listed in Table 1 confirms the structure deduced above. Reflections required to be absent by the symmetry are omitted from the table. The slightly low values observed for the first few lines are probably the result of absorption in the sample.