

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1956). **9**, 191

The probability distribution of X-ray intensities: atoms in special positions. By A. HARGREAVES,
Physics Department, College of Technology, Manchester 1, England

(Received 20 October 1955 and in revised form 23 November 1955)

Useful information about the symmetry of a structure may be provided by the probability distribution of the intensities of its X-ray reflexions. Centrosymmetrical and non-centrosymmetrical structures give rise to different distributions, represented by $(\bar{1})N(Z)$ and $(1)N(Z)$, when the unit cell contains a sufficient number of atoms distributed effectively at random (Wilson, 1949; Howells, Phillips & Rogers, 1950). Hargreaves (1955) has shown that the crystal symmetry modifies the intensity distribution in a more complex fashion when the scattering power of a single heavy atom in a general position in the unit cell dominates that of the remaining lighter atoms. He has considered the intensity distributions of zones of reflexions which provide information about the symmetry of the nine oblique and rectangular plane groups and finds that they are of three different types. These three types, designated by $(\text{max.})N(Z)$, $(C)N(Z)$ and $(CC)N(Z)$, are quite different from the distributions $(\bar{1})N(Z)$ and $(1)N(Z)$.

In a recent paper Collin (1955) considers the effect on the intensity distributions of atoms in fixed positions, an atom in a fixed position being defined as one which has no variable position parameter. Collin shows that the $(1)N(Z)$ and $(\bar{1})N(Z)$ distributions are seriously modified when the atoms in fixed positions are heavy compared with the other atoms in the structure, and that the distribution curve for centrosymmetrical structures becomes $(\text{max.})N(Z)$ if the atom in the fixed position is very heavy. Collin states that it is difficult to relate his own work on atoms in fixed positions to that of Hargreaves, which is concerned with atoms in general positions, because in one case (Collin) the reflexions are divided into groups, each with its characteristic $N(Z)$ function, whilst in the other (Hargreaves) all reflexions are considered together.

The reason why it is possible to consider all reflexions together (excluding, in general, those for which h or $k = 0$) when the heavy atoms are in general positions is that, for each of the nine plane groups examined, all types of hk reflexions give rise to the same $N(Z)$ distribution. For example, in the plane group pmg the reflexions may be divided into two groups—those with h even and those with h odd; the geometrical structure factor is $4 \cos 2\pi hx \cdot \cos 2\pi ky$ for the first group and $-4 \sin 2\pi hx \cdot \sin 2\pi ky$ for the second group: but for an atom in a general position both expressions lead to the same distribution, namely $(CC)N(Z)$.

It is implicit within the earlier paper by the author that reflexions of types $h0$ and $0k$ must, in general, be considered separately from those of type hk . Thus if hk reflexions have a geometrical structure factor of the form

$G(hk) = \cos 2\pi hx \cdot \cos 2\pi ky$, then the distribution is $(CC)N(Z)$; the corresponding $h0$ and $0k$ reflexions have $G(h0) = \cos 2\pi hx$ and $G(0k) = \cos 2\pi ky$ respectively, and therefore the $(C)N(Z)$ distribution. And if hk reflexions have geometrical structure factors of the form either $G(hk) = \cos 2\pi(hx + ky)$ or $G(hk) = \cos 2\pi hx$, then the distribution is $(C)N(Z)$; when $h = 0$, $\cos 2\pi(hx + ky)$ reduces to $G(0k) = \cos 2\pi ky$ and the axial reflexions still have the $(C)N(Z)$ distribution, but $\cos 2\pi hx$ reduces to $G(0k) = 1$ (unity) and the axial reflexions then have the $(\text{max.})N(Z)$ distribution. It is evident, therefore, that making h or $k = 0$ may modify the geometrical structure factor so as to produce a different type of distribution. Similar modifications of the geometrical structure factor, giving different $N(Z)$ distributions, are obtained by making x or $y = 0, \frac{1}{2}, \frac{1}{4}$ etc., and in the following it will be shown that the work of Hargreaves (1955) can easily be extended to cover single heavy atoms in special (including fixed) positions. It will be seen that it is then no longer invariably the case that the same $N(Z)$ distribution is given by the different groups of reflexions as-

Table 1

Plane group	Symmetry of special position	Type of intensity distribution
$p1$	None	—
$p2$	2	$(\text{max.})N(Z)$
pm	m	$(\text{max.})N(Z)$
pg	None	—
cm	m	$(\text{max.})N(Z)$
pmm	m	$(C)N(Z)$
	mm	$(\text{max.})N(Z)$
pmg	m	$(C)N(Z)$
	2	$(\text{max.})N(Z)$ when h even $(\bar{1})N(Z)$ when h odd
pgg	2	$(\text{max.})N(Z)$ when $(h+k)$ even $(\bar{1})N(Z)$ when $(h+k)$ odd
mmm	m	$(C)N(Z)$
	2	$(\text{max.})N(Z)$ when h even $(\bar{1})N(Z)$ when h odd
	mm	$(\text{max.})N(Z)$
$p4$	2	$(\text{max.})N(Z)$ when $(h+k)$ even $(\bar{1})N(Z)$ when $(h+k)$ odd
	4	$(\text{max.})N(Z)$
$p4m$	m	$(CC)N(Z)$
	mm	$(\text{max.})N(Z)$ when $(h+k)$ even $(\bar{1})N(Z)$ when $(h+k)$ odd
	$4mm$	$(\text{max.})N(Z)$
$p4g$	m	$(CC)N(Z)$
	mm	$(\text{max.})N(Z)$ when $(h+k)$ even $(\bar{1})N(Z)$ when $(h+k)$ odd
	4	$(\text{max.})N(Z)$ when $(h+k)$ even $(\bar{1})N(Z)$ when $(h+k)$ odd

sociated with a given plane group. For certain reflexions the contribution of the heavy atom becomes nil; the distribution is then determined by the lighter atoms, and becomes $(\bar{1})N(Z)$ (for the plane groups considered) if these atoms are arranged at random and have similar atomic scattering factors.

Table 1 indicates the distributions obtained when the heavy atom is placed in any special position in the oblique, rectangular and square plane groups; the special positions include those with no variable parameters (the fixed positions of Collin) and mirror planes, which have one fixed and one variable parameter. Hexagonal plane groups are omitted from Table 1 because the special positions with one variable parameter appear to be represented by new types of distribution whilst those with fixed parameters are represented by variants of $(\text{max.})N(Z)$ which cannot be tabulated in compact form. The method of deriving the results given in Table 1 is illustrated by taking as an example the plane group pmg to which reference has already been made.

Plane group pmg

(i) Heavy atom at general position (x, y)

The geometrical structure factor is $4 \cos 2\pi hx \cdot \cos 2\pi ky$, when h is even, and $-4 \sin 2\pi hx \cdot \sin 2\pi ky$ when h is odd; both types of reflexions will therefore have the intensity distribution $(CC)N(Z)$ (Hargreaves, 1955).

(ii) Heavy atom at special position $(\frac{1}{2}, y)$ on m

The geometrical structure factor reduces to $\pm 4 \cos 2\pi ky$ when h is even, and $\pm 4 \sin 2\pi ky$ when h is odd; the

intensity distribution for both types of reflexions is now $(C)N(Z)$ (Hargreaves, 1955).

(iii) Heavy atom at special position $(0, 0)$ or $(0, \frac{1}{2})$ on 2

When h is even the geometrical structure factor becomes unity and the corresponding intensity distribution is $(\text{max.})N(Z)$ (Hargreaves, 1955). When h is odd the geometrical structure factor becomes zero; the heavy atom then makes no contribution to the reflexions and the intensity distribution, determined by the lighter atoms, is $(\bar{1})N(Z)$ (Wilson, 1949; Howells *et al.*, 1950).

The distributions listed in Table 1 are strictly valid only when the atoms in special positions are sufficiently heavy to dominate completely the remaining lighter atoms; but even when the atoms in special positions are only moderately heavy, Table 1 should still be useful in indicating the general nature of the deviations to be expected from the $(1)N(Z)$ or $(\bar{1})N(Z)$ distributions. Table 1 may be used both as an aid in determining crystal symmetry and (in some cases) for distinguishing between different possible special positions.

References

- COLLIN, R. L. (1955). *Acta Cryst.* **8**, 499.
 HARGREAVES, A. (1955). *Acta Cryst.* **8**, 12.
 HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
 WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318.

Acta Cryst. (1956). **9**, 192

Note on the crystal structure of sodium dichromate dihydrate. By J. A. CAMPBELL, *Oberlin College, Oberlin, Ohio, U.S.A.*

(Received 7 November 1955)

Studies of the adsorption spectra of aqueous solutions of chromates and dichromates in connection with the equilibria found therein have shown that the spectra of dichromate and acid chromate ions are similar, and close to those of the solid dichromates. This raises the point as to whether certain solid dichromates contain acid chromate ions rather than dichromate ions. Inspection of the structure of sodium dichromate dihydrate, formula $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, was undertaken in an attempt to settle the question for a particular crystal where the alternatives were possible. (It could have the formula $\text{Na}_2(\text{HCrO}_4)_2 \cdot \text{H}_2\text{O}$.)

Rotation photographs about all three axes and Weissenberg photographs about two axes (a and b) were taken. The crystals, grown from water solution at room temperature, were monoclinic with unit-cell dimensions:

$$a = 6.05, b = 10.5, c = 12.6 \text{ \AA}, \beta = 94.9^\circ.$$

These cell dimensions, a density of 2.52 g.cm.^{-3} , and a formula weight of 298 g./mole gave $n = 4.06$. Analysis of the photographs showed systematic absences for $0k0$

when $k = 2n$, indicating a space group of either $P2_1$ or $P2_1/m$. The crystal showed no piezoelectricity, and the response to the liquid-air test for pyroelectricity was doubtful. Wilson's method indicated the crystal to be centric, so that the space group must be $P2_1/m$.

Patterson diagrams were prepared from the two Weissenbergs. Analysis indicated that the chromiums were paired and located in the mirror planes. No detailed analysis has been, or will be, made. A Cr-Cr distance of about 3.2 \AA and a Cr-O-Cr angle of about 120° are possible. The additional work necessary to complete the structure does not seem justified from my own point of view, since no structures with independent chromiums, i.e. HCrO_4^- groups, were discovered which satisfied the data.

I wish to thank Miss Helen Megaw for considerable advice while the photographs were being taken, Dr W. H. Taylor for making available the facilities of the Cavendish X-ray laboratory, and Dr S. Bailey for aid in running the Pattersons on the IBM machines at the University of Wisconsin.