

$\pm 0.00008 \text{ \AA}$. The value of the displacement appears to be larger below the Néel temperature but it is not significantly greater than the accuracy of the measurements. Further, the displacement might reasonably be expected to increase as the temperature is reduced below the Néel point, whereas the observed displacement showed no tendency to do so and in fact the room temperature value was about three times that obtained at -102°C .

To investigate the broadening effect for a powdered chromium specimen the 310 reflexion for Cu $K\alpha$ radiation was recorded with an X-ray diffractometer. The integral breadth of the reflexion was measured for 20 recordings in a range (40 to 70°C) above the Néel point, and below the Néel point for 21 recordings in the range 15 to 40°C and 6 in the range -70 to -40°C . The mean values of the breadth for all three ranges lie within 0.8%, the values in the higher and lower ranges being slightly larger than the values in the middle range. This latter indicates that the small observed broadening is more likely to be due to slight thermal instability than to a splitting of the reflexion.

The above results do not weight the argument in favour of the overall cubic symmetry of antiferro-

magnetic chromium but together with the previous discussion they point to an upper limit for Δ , in the specimens examined, of about 10^{-5} , where Δ is defined in the relation $a=c(1+\Delta)$ for the distorted structure.

The author wishes to thank Professor G. E. Bacon for helpful discussions throughout this work.

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Monoclinic Diffraction Patterns Produced by Certain Triclinic Crystals and Diffraction Enhancement of Symmetry

BY R. SADANAGA AND HIROSHI TAKEDA

Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo, Tokyo, Japan

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The triclinic mica polytype $10Tc_3$ produces an X-ray diffraction pattern monoclinic in symmetry. It is now established that if a triclinic structure, with a metrically monoclinic lattice, is composed of two kinds of layer, one being an integral multiple, in thickness, of the other and each bearing twofold rotational symmetry, its diffraction pattern should assume a rigorously monoclinic symmetry. The term *diffraction enhancement of symmetry* is proposed for phenomena of this kind. Some triclinic mica polytypes, though not in conformity with the above conditions, still give rise to diffraction patterns monoclinic in a very good approximation, and these cases are specified as *quasi-enhancement*. If the X-ray diffraction pattern of a crystal bears, only in part, a symmetry higher than that of the crystal, the case is designated *partial enhancement*.

Introduction

It has often been observed that some sets of X-ray reflections from a crystal exhibit, besides the centrosymmetry due to the Friedel law, a symmetry higher than that of the crystal. One of the notable examples is a case of triclinic wollastonite (Ito, 1950). It gives the *b*-axis rotation photograph in which spots on the even-order layer-lines are arranged, in intensity as well as position, quite symmetric against the zero layer. As far as these reflections are concerned, therefore, the pattern strictly assumes an appearance of that of a monoclinic

symmetry, though those on the odd-order layer-lines betray that the symmetry of the crystal is in fact triclinic. Boléite and monoclinic trinitrotoluene also exhibit features similar to the above in their X-ray patterns, some sets of reflections being strictly cubic in the former in spite of its tetragonal symmetry and orthorhombic in the latter.

These intricate phenomena have been dealt with by Ito (1950), who has given explanations of these based upon his theory of twinned space groups. In fact, in each of these examples, it has been confirmed experimentally that the crystal is a polysynthetic twin of a

certain unit that has within itself its own symmetry higher than the space-group symmetry of the whole scheme of the crystal structure. Let us imagine a triclinic crystal having hexagonal molecules of one kind arranged according to its crystal lattice. In this case, just as in those of hexamethylbenzene (Lonsdale, 1928, 1929; Brockway & Robertson, 1939) and hexachlorobenzene (Lonsdale, 1931), there will in general be no special correlation between the molecular orientation and the crystal lattice, and accordingly the symmetry of the molecule will not render any direct influence upon the symmetry of the X-ray diffraction pattern in so far as the normal Bragg reflections are concerned. On the other hand, in every case of polysynthetic twins mentioned above, owing to the orientational relation inherent in twinning between twin operation and symmetry of the unit, a certain correlation appears between the symmetry of the unit and the resulting twinned lattice, thus impressing the symmetry of the unit upon certain sets of reflections.

During the course of recent investigations of a series of mica polytypes, however, one of us came across a case in which a triclinic polytype designated $10Tc_3$ produces an X-ray diffraction pattern strictly monoclinic in its every aspect (Ross, Takeda & Wones, 1966). Since the structure of the polytype determined turned out to be triclinic in symmetry, we started an investigation to ascertain whether it was at all possible for a triclinic structure to exhibit a diffraction pattern rigorously monoclinic in symmetry, and we found that not only is this indeed true for a certain type of layer structure including the $10Tc_3$ mica polytype but also it is approximately realized in other mica polytypes such as the eight-layer ones to be discussed below.

Theoretical considerations and diffraction enhancement of symmetry

Suppose that a crystal structure is composed of parallel layers of r kinds satisfying the conditions:

(1) Every layer possesses a twofold rotational symmetry whose axis is parallel to the layer and to a certain direction which is to be taken as the b axis of the crystal,

(2) These layers are so juxtaposed that their respective origins are arranged along a line perpendicular to the b axis. Therefore, if the c axis is taken parallel to this line and the a axis parallel to the layer and per-

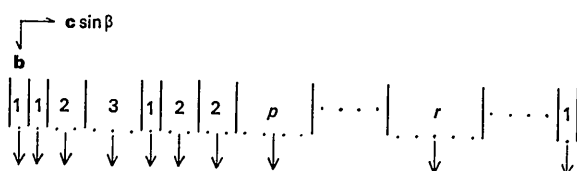


Fig. 1. Example of the structure satisfying the four conditions in the text. Projection along the a axis. The thickness of each layer is an integral multiple of that of layer 1. Arrows show partial twofold axes. Dots along the bottom of layers indicate intervals of $1/M$ of the period along the direction perpendicular to the layers.

pendicular to the b axis, a set of metrically monoclinic axes will be established in the structure,

(3) There is, in the order of stacking of those layers, no symmetry other than the repetition according to the periodicity along the c axis, and

(4) The thickness of any one of the kinds of layer is an integral multiple of the thickness of the thinnest kind. This condition includes the case in which the structure consists of layers of r kinds, but all of equal thickness.

An example of the structure defined above is illustrated in Fig. 1 in a projection along the a axis, where each of the layers denoted by 2, 3, ... r is an integral multiple, in thickness, of the layer denoted by 1. Although every layer has a twofold axis in the middle, owing to condition (3), the operations of the axis are effective only within a certain set of layers; these are therefore partial symmetry operations or λ -operations after the definitions by Dornberger-Schiff (1956, 1964), and are not qualified to be overall symmetry operations in the space group of the structure. Therefore, the symmetry of the structure is triclinic in spite of its apparently monoclinic lattice.

Now, let $d_1(x, y, z), d_2(x, y, z), \dots, d_r(x, y, z)$ be the electron-density functions for the respective layers, and $F_1(u, v, w), F_2(u, v, w), \dots, F_r(u, v, w)$, the corresponding Fourier transforms. Then, one of the latter, say $F_p(u, v, w)$, is expressed by

$$F_p(u, v, w) = \int d_p(x, y, z) \exp 2\pi i(ux + vy + wz) dV,$$

where dV is the volume element at (x, y, z) in direct space. Because of the twofold rotational symmetry of the p -layer [condition (1)], $F_p(u, v, w)$ can be written as

$$F_p(u, v, w) = 2 \int d_p(x, y, z) \cos 2\pi(ux + wz) \exp 2\pi i(vy) dV = F_p(\bar{u}, v, \bar{w}), \quad (1)$$

where the origin is taken on the twofold axis. Therefore, $F_p(u, v, w)$ is complex in respect to vy only, and may accordingly be expressed as

$$F_p(u, v, w) = F_p(\bar{u}, v, \bar{w}) = f_R \cos 2\pi(vy) + if_R \sin 2\pi(vy) = A_p + iB_p, \quad (2)$$

where f_R is a real function of u, w, x and z .

Then, in conformity with condition (2), the electron-density function, $d(x, y, z)$, of the structure runs,

$$d(x, y, z) = \sum_{p=1}^r \{d_p(x, y, z) * \sum_j \delta(z - z_{p,j})\},$$

where δ represents a delta function, $z_{p,j}$ the z coordinate of the j th p -layer, and the asterisk stands for the convolution of the two functions on its both sides. The Fourier transform, $F(u, v, w)$, of $d(x, y, z)$ is given by

$$F(u, v, w) = \sum_{p=1}^r \{F_p(u, v, w) \times \int_j \delta(z - z_{p,j}) \exp 2\pi i(wz) dz\}. \quad (3)$$

If we normalize these δ functions so that their peak values are all equal to 1, we can deduce the transform of their sum as follows,

$$\int_j \Sigma \delta(z - z_{p,j}) \exp 2\pi i(wz) dz = \Sigma \int_j \delta(z - z_{p,j}) \exp 2\pi i(wz) dz = \Sigma \exp 2\pi i(wz_{p,j}). \quad (4)$$

Putting (4) in (3), we obtain for the case, $w=l$,

$$F(u, v, l) = \sum_{p=1}^r \{F_p(u, v, l) \times \Sigma \exp 2\pi i(lz_{p,j})\}. \quad (5)$$

Expressing the sum of exponential functions by $\alpha_p + i\beta_p$ and using (2), we can rewrite the above equation as

$$\begin{aligned} F(u, v, l) &= \sum_{p=1}^r \{(A_p + iB_p)(\alpha_p + i\beta_p)\} \\ &= \sum_{p=1}^r \{(A_p \alpha_p - B_p \beta_p) + i(B_p \alpha_p + A_p \beta_p)\}. \end{aligned} \quad (6)$$

Similarly, we obtain

$$F(\bar{u}, v, \bar{l}) = \sum_{p=1}^r \{(A_p \alpha_p + B_p \beta_p) + i(B_p \alpha_p - A_p \beta_p)\}. \quad (7)$$

If the difference, D , of the squared absolute value of $F(\bar{u}, v, \bar{l})$ from that of $F(u, v, l)$ is taken,

$$\begin{aligned} D &= |F(u, v, l)|^2 - |F(\bar{u}, v, \bar{l})|^2 \\ &= \left(\sum_{p=1}^r A_p \alpha_p - \sum_{p=1}^r B_p \beta_p \right)^2 + \left(\sum_{p=1}^r B_p \alpha_p + \sum_{p=1}^r A_p \beta_p \right)^2 \\ &\quad - \left(\sum_{p=1}^r A_p \alpha_p + \sum_{p=1}^r B_p \beta_p \right)^2 - \left(\sum_{p=1}^r B_p \alpha_p - \sum_{p=1}^r A_p \beta_p \right)^2 \\ &= -4 \sum_{p=1}^r \sum_{q=1}^r \alpha_p \beta_q A_p B_q + 4 \sum_{p=1}^r \sum_{q=1}^r \alpha_q \beta_p A_p B_q \\ &= 4 \sum_{p=1}^r \sum_{q=1}^r A_p B_q (\alpha_q \beta_p - \alpha_p \beta_q), \end{aligned} \quad (8)$$

and D is in general not zero.

Now, we introduce condition (4). Since the thickness, t_p , of the p -layer is an integral multiple of t_1 of the thinnest 1-layer, the period of the structure perpendicular to the layers must also be an integral multiple of the latter, and let the period be $M \times t_1$, M being integral. Then, according to the equality,

$$\sum_{m=0}^{M-1} \exp 2\pi i \left(l \frac{m}{M} \right) = 0, \quad (9)$$

where $l (\neq 0)$, m and M are all integers, the relation holds:

$$\sum_{p=1}^r \sum_j \Sigma \exp 2\pi i \left\{ l \left(z_{p,j} \pm \frac{n_p}{2M} \right) \right\} = 0. \quad (10)$$

In equation (10), the origin of the structure is taken as coinciding with that of one of the thinnest layers, namely, on its twofold axis, and as will be recognized in Fig. 1, when $t_p = N_p \times t_1$, $n_p = 1, 3, 5, \dots, N_p - 1$ if the

layer is of an even N_p , and $n_p = 0, 2, 4, \dots, N_p - 1$ if the layer is of an odd N_p .

The relation (10) is rewritten as,

$$\begin{aligned} \sum_{p=1}^r \left\{ \Sigma \exp 2\pi i(lz_{p,j}) \times \Sigma \exp 2\pi i \left(\pm l \frac{n_p}{2M} \right) \right\} \\ = \sum_{p=1}^r \left\{ K_p \Sigma \exp 2\pi i(lz_{p,j}) \right\} = 0, \end{aligned} \quad (11)$$

where

$$K_p = 2 \sum_{n_p=1}^{N_p-1} \cos 2\pi \left(l \frac{n_p}{2M} \right)$$

for an even N_p , and

$$K_p = 1 + 2 \sum_{n_p=2}^{N_p-1} \cos 2\pi \left(l \frac{n_p}{2M} \right)$$

for an odd N_p . In any case, the K_p 's are all real and even functions of l . From (11) and because $K_1 = 1$, therefore, the sum of the exponential terms for the thinnest 1-layer is explicitly expressed by those for the other layers as

$$\Sigma \exp 2\pi i(lz_{1,j}) = - \sum_{p=2}^r \{ K_p \Sigma \exp 2\pi i(lz_{p,j}) \}$$

or

$$\alpha_1 + i\beta_1 = - \sum_{p=2}^r K_p (\alpha_p + i\beta_p)$$

for positive l 's and

$$\alpha_1 - i\beta_1 = - \sum_{p=2}^r K_p (\alpha_p - i\beta_p)$$

for negative l 's.

Introduction of these relations into (8) produces no special result, D being not zero as before. However, in the case of $r=2$, that is, if the structure is composed of two kinds of layer, one being an integral multiple, in thickness, of the other, the relation holds:

$$\alpha_1 \pm i\beta_1 = -K_2(\alpha_2 \pm i\beta_2),$$

and accordingly

$$\alpha_1 = -K_2\alpha_2 \quad \text{and} \quad \beta_1 = -K_2\beta_2.$$

Putting these into (8), we derive

$$D = 4K_2(A_1B_2 - A_2B_1)(\alpha_2\beta_2 - \alpha_2\beta_2) = 0; \quad (12)$$

i.e.

$$|F(u, v, l)|^2 = |F(\bar{u}, v, \bar{l})|^2,$$

provided $l \neq 0$, which is prerequisite to the equality (9).

On the other hand, when $l=0$, we obtain from (5)

$$F(u, v, 0) = \sum_{p=1}^r F_p(u, v, 0),$$

and since every $F_p(u, v, l)$ and accordingly every $F_p(u, v, 0)$ is digonally symmetric with respect to the b^* axis as seen from (1), we derive

$$F(u, v, 0) = F(\bar{u}, v, 0)$$

and accordingly

$$|F(u, v, 0)|^2 = |F(\bar{u}, v, 0)|^2.$$

We thus arrive at the conclusion that, if a crystal structure is composed of two kinds of layer satisfying the conditions previously mentioned, the absolute values of its Fourier transform are digonally symmetric with respect to the b^* axis, though not everywhere in reciprocal space but only in the set of parallel planes with integral w coordinates, while the phase angles are asymmetric everywhere as will be recognized from (6) and (7), both for the case in which $r=2$. This means that the crystal, in spite of its triclinic symmetry, gives the hkl reflection and its counterpart, $\bar{h}k\bar{l}$, always an equal intensity, thus producing the X-ray diffraction pattern rigorously monoclinic in symmetry.

The phenomenon described here is similar to those due to the Friedel law in the respect that, owing to the lack of information about the phase angle, the symmetry of a crystal as deduced direct from ordinary diffraction experiments is sometimes higher than the true symmetry of the crystal. As more examples of a similar kind are expected to be discovered in future, it may be appropriate to specify them with a suitable name, and we propose the term *diffraction enhancement of symmetry* for the phenomenon that the X-ray diffraction pattern of a crystal exhibits, besides the centrosymmetry due to the Friedel law, a symmetry higher than that of the crystal.

Examples of diffraction enhancement among mica polytypes

The structure of every mica polytype consists of monoclinic unit-layers having the symmetry of $1C2/m$ [nota-

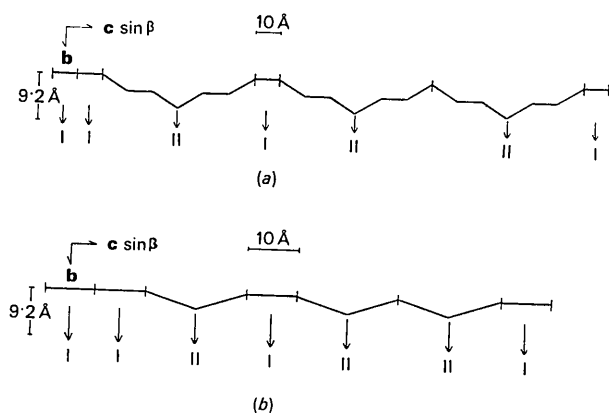


Fig. 2. (a) Fictitious 22-layer triclinic mica polytype to produce a monoclinic diffraction pattern. The diagram shows a Smith-Yoder diagram projected along the a axis. Each segment of line starts from a potassium ion in a unit-layer and ends at another in the next unit-layer. I and II signify two kinds of layer. (b) Smith-Yoder diagram of the ten-layer triclinic mica polytype $10Tc_3$ projected along the a axis.

tion after A. Niggli (Wood, 1964)], the mode of stacking of the unit-layers varying from one polytype to another. In general the structure of a polytype contains such unit-layers arranged, though not necessarily successively to one another, after the manner of the layer-sequence in the one-layer monoclinic mica, $1M$ (Smith & Yoder, 1956), and a series of these unit-layers will be called in this paper *normal layers*. The other layers in the structure, which owing to rotations about axes perpendicular to the layers, depart from the $1M$ sequence, will be named *abnormal layers*.

Then, if the structure of a triclinic mica polytype with a metrically monoclinic crystal lattice comprises sets of unit-layers, all the sets being equal to one another in configuration, and each containing some abnormal layers and carrying in the middle a twofold rotation axis in the direction parallel to the b axis of the crystal, and if the rest of the structure is constituted solely with normal layers, the X-ray diffraction pattern given by this polytype is accurately monoclinic in symmetry. In fact, if we designate the sets containing abnormal layers *digonal sets* because of their twofold rotational symmetry, we can easily recognize that the origins of these digonal sets as well as those of normal layers in the polytype can be so chosen as to be located along a line parallel to the c axis. By denoting the electron-density functions for a normal layer and a digonal set by $d_1(x, y, z)$ and $d_2(x, y, z)$ respectively, we shall see that the argument expounded in the foregoing section applies to this case. A fictitious example of such a polytype is illustrated in Fig. 2(a) in a Smith-Yoder diagram projected along the a axis.

Although an infinite number of triclinic mica polytypes satisfying the above conditions is conceivable, the only example so far brought to light experimentally is the one designated $10Tc_3$. This polytype discovered by Ross & Wones (1965) was described by them as a ten-layer monoclinic one from its X-ray diffraction pattern, but subsequent studies have disclosed that, though the symmetry of the pattern is indeed monoclinic, no sequence of layer-stacking in that symmetry satisfies the intensity distribution of the X-ray diffraction pattern, and the final structure deduced is a triclinic one as shown in Fig. 2(b) (Ross, Takeda & Wones, 1966). In fact, if the digonal sets are so chosen as indicated by II in the Figure, it will be obvious that this polytype produces a diffraction pattern which is rigorously monoclinic in symmetry.

Quasi-enhancement

If a triclinic mica polytype contains more than one kind of digonal set, *i.e.* consists of more than two kinds of layer including normal layers, equation (12) does not hold for this case and the symmetry of its diffraction pattern should be true to that of the crystal, namely triclinic. However, even in this case, some polytypes may still give rise to diffraction patterns monoclinic in symmetry, even though not so accurately as before

yet certainly to a very good approximation. We shall call this case *quasi-enhancement*; we begin the discussion with some examples.

Among eight-layer mica polytypes theoretically predicted, there are some whose layer sequences are as given in Fig. 3(a). All of these polytypes comprise rotations of the unit-layers only by $\pm 120^\circ$ about the c^* axis, and are triclinic. As recognized in the Figure, throughout these examples, there exist two kinds of digonal set, each having a configuration different from the other. In spite of this fact, however, calculations of their periodic intensity distribution functions (Takeda, 1967) suggested that every one of these should produce a diffraction pattern monoclinic in symmetry. In order to understand this situation, let us convert the unit-layer from the conventional one, which has its lateral dimension from one layer of alkali ions to another, to a new one from the middle of an octahedral layer to that of the next one. The new unit-layer thus chosen has a layer of alkali ions in the middle and those of octahedral cations on its both sides. The advantage of assuming the unit-layer like this lies in the following two facts. Firstly, for the trioctahedral micas, it has been empirically established (Donnay, Donnay & Takeda, 1964) that atoms in this new unit-layer are arranged, to a very good approximation, after the ditrigonal symmetry of $1P\bar{3}1m$ [notation after A. Niggli, (Wood, 1964)]. Secondly, because of this choice of unit layer, if the structure of a polytype comprises, in the stacking of the conventional unit layers, only $\pm 120^\circ$ rotations about the c^* axis, it will be re-described as a stacking of the new unit layers, all in parallel orientation but with translations of layers by $-\frac{1}{3}\mathbf{a}$ with respect to the neighbouring layers, where \mathbf{a} is a vector representing a period along one of the three axes of the hexagonal mesh in the unit layer. In fact, this relation between layers greatly facilitates the deduction of information useful for the present purpose, and through this change of unit layers the Smith-Yoder diagrams in Fig. 3(a) stand as they are, provided the vectors be now reinterpreted as representing the translations of successive layers.

Now, upon this change of unit layers, the structure of any one of those polytypes in Fig. 3(a) will be considered as consisting of two kinds of layer, the two kinds nevertheless being identical with each other in structure as well as in thickness, one being shifted with respect to the other along the axis perpendicular to the direction of the stacking, as illustrated in Fig. 3(b). Note that in spite of the change of unit layers, we still keep the same axial setting as that of the one-layer monoclinic mica. With this axial setting, layers of one kind have no shift along the b axis. These layers are what have been called *normal layers* in the previous section. Those of the other kind have their shift vectors of $+\frac{1}{3}\mathbf{b}$. Then, because each of these layers has a twofold rotation axis parallel to the b axis, the symmetry of the diffraction pattern of any of these polytypes is monoclinic to the same extent of approxima-

tion as the structure of the unit layer can be regarded as being of the ditrigonal symmetry $1P\bar{3}1m$.

It is interesting to know how many such polytypes giving quasi-enhancement are possible for a given total layer number for those polytypes which comprise rotations of the conventional unit-layers only by 0° and $\pm 120^\circ$ about the c^* axis. No such polytype is found among those with layer numbers less than six, one is found out of 39 possible seven-layer polytypes (excluding those of enantiomorphic ones), 4 out of 94 eight-layer ones, and 18 out of 572 ten-layer ones.

Partial enhancement

As mentioned at the beginning of this paper, the X-ray diffraction pattern of a crystal often bears, only in part, a symmetry higher than that of the crystal, and such

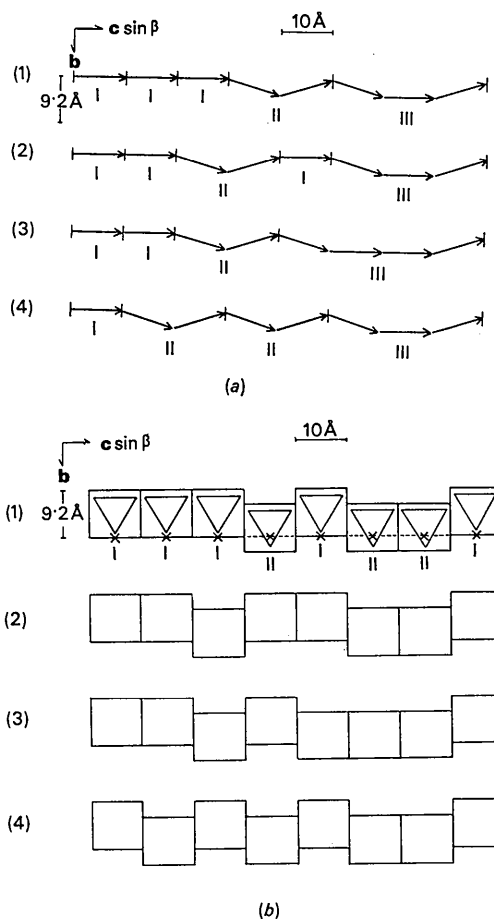


Fig. 3. (a) Eight-layer triclinic mica polytypes theoretically predicted, in Smith-Yoder diagrams projected along the a axes. These polytypes are composed of three kinds of layer I, II and III, but expected to show 'quasi-enhancement'. (b) Structural schemes of the polytypes in Fig. 3(a) after the change of unit layers as described in the text. Note that every one of these consists of two kinds of layer, one being shifted in the b direction from the other. The electron-density distribution and the origin of each of the layers I and II in (1) are illustrated by a triangle and a cross respectively.

a case will be defined as *partial enhancement*. The reflections displaying the higher symmetry are distributed in the pattern after a certain symmetry and are usually those in which one or more than one index is a multiple of an integer. For example, in the case of triclinic wollastonite, the *hkl* reflection, when *k* is even (a multiple of 2), is equal in intensity to, and located symmetrical against the *h0l* plane with, the $(h+k)/2, \bar{k}, l$ reflection (Ito, 1950).

Introductory remarks on partial enhancement have been published (Sadanaga, 1959, 1963) and the detailed theory will be treated shortly elsewhere.

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A Simple Theory of the Off-Centre Displacement of Cations in Octahedral Environments

BY HELEN D. MEGAW

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

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Off-centre displacement occurs when the effective size of a cation B is such that the unstressed B–O bond length is less than $1/\sqrt{2}$ times the oxygen ‘diameter’. Assuming that all interatomic forces are central, there is then, for a symmetrically placed cation, a tension in the O–B–O diameters and a compression in the O–O edges of the octahedron. Elementary Born-theory treatment shows that for an isolated octahedron the tension will be relaxed by off-centre displacement of B. The relaxation will be shared with the O–O edges, which are therefore elongated. Relaxation can affect one, two, or three O–B–O diameters simultaneously, with different consequences for the edge lengths. The character and magnitude of the relaxation are independent of the symmetry and the structure, depending only on the B displacement. Predictions have been verified by experimental evidence from the structures and lattice parameters of KNbO₃ and NaNbO₃. Quantitatively, the off-centring must be strongly influenced by polarization (involving non-central forces), which is also the means whereby effects within octahedra are communicated to their neighbours. Qualitatively, however, when the displacements are fairly small (as is true for Nb) the present description in terms of bond stresses is useful and allows predictions to be made. A further paper on thermal expansion is planned.

Interest in the off-centre displacements of ‘cations’ in octahedra has been stimulated by their important role in ferroelectrics of the perovskite type. That the cause of the displacement is not specific to ferroelectrics, but is more generally rooted in crystal chemistry, is now recognized. It has been discussed by Orgel (1958), who showed that it depended on the effective radius (not the conventional ionic radius) of the cation B relative to that of oxygen. The present note derives the same conclusion in a slightly different way, which allows predictions to be made about the character of the octahedral distortion in relation to the type and magnitude of the off-centre displacement.

The Born theory, in its simplest form, assumes that the equilibrium distance between two atoms depends only on the potential energies of their mutual attractive

and repulsive forces, and that the equilibrium distance is that for which the force on either atom is zero, *i.e.* the bond is unstressed. In crystal structures (as distinct from diatomic molecules) this cannot be true. Consider the octahedron as an isolated unit (a reasonable next approximation). There are repulsions in each of the O–O edges, and these produce tensions in each of the diametral O–B–O links (Fig. 1). Hence, even for a central B atom, the B–O bonds are elongated beyond their ‘unstressed’ length (a length which cannot be derived directly from measured interatomic distances, since all of these represent more or less stressed conditions, but which is a useful concept in discussion).

The O–O repulsions are partly electrostatic, partly of covalent origin. The ionic part varies slowly with O–O distance, but is always relatively weak. The co-