

## Studies in Domain Crystallography

### III. The Use of Composite Reciprocal-Lattice Theory to Investigate the Transition in Potassium Nitrite at About 40°C

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After a thermal cycle traversing the transformation temperature range to the high temperature form I, a single crystal of potassium nitrite form II is converted into a hybrid crystal composed of domains of structure II in specific orientations. A detailed interpretation of some oscillation photographs of such a hybrid crystal in terms of its composite reciprocal lattice demonstrates that the domain orientations are related by the point-group symmetry  $m\bar{3}$ . It is therefore concluded from this study of a hybrid crystal of form II that form I must be cubic.

Consideration of the atomic displacements involved in the transformation  $\text{II} \rightleftharpoons \text{I}$  show these to be consistent with a sodium chloride structure for form I, and it is concluded that the lower cubic symmetry controlling domain orientations arises because of the physical requirement for domains to coexist within the envelope of a 'single' crystal.

#### Introduction

The transformation in the structure of potassium nitrite at around 40°C was first demonstrated by dilatometry and ultraviolet spectroscopy (Cleaver, Rhodes & Ubbelohde, 1963; Hazlewood, Rhodes & Ubbelohde, 1963). An X-ray investigation of this transition (Parry, Schuyff & Ubbelohde, 1965) has confirmed that a single crystal of the room temperature form, II, transforms continuously into the high temperature form, I, while the reverse transformation,  $\text{I} \rightarrow \text{II}$  gives rise to a hybrid single crystal composed of domains of II in specific orientations. It is the purpose of the present paper to examine more closely the crystallographic aspects of the transition with particular emphasis on the structural changes involved.

Single crystals of I formed directly from II are strained and attempts to anneal them have so far been unsuccessful or have led to the loss of most of the crystal by evaporation. It is considered that a full structural investigation of form I will require a single crystal to be grown above the transition temperature. This has not yet been attempted but may prove to be difficult, for the existence of polymorphic alternatives can impair regular growth (*cf.* Menary, Ubbelohde & Woodward, 1951). Therefore, the procedure adopted for investigating the symmetry of I has been to examine the composite reciprocal lattice symmetry of II. The results indicate that I is cubic with the oxygen atoms of the nitrite group positionally disordered around the anion sites in a sodium chloride type structure. The lowering of the transformation symmetry from that expected from the sodium chloride structure ( $m\bar{3}m$ ) to that actually found ( $m\bar{3}$ ) is attributed to the requirements of domain coexistence.

#### Previous structural investigations

The room temperature form II has been studied crystallographically by Ziegler (1936). It was found to be monoclinic, with cell dimensions  $a_{\text{II}}=4.45$ ,  $b_{\text{II}}=4.99$ ,  $c_{\text{II}}=7.31\text{kX}$ ,  $\beta_{\text{II}}=114^\circ 50'$ ; this cell contains two formula units  $\text{KNO}_2$ . The space group was not uniquely determined by systematic absences, but the assignment  $Cm$  led to a structure which gave qualitative agreement between observed and calculated structure factors. The final atomic parameters were

	$x_{\text{II}}$	$y_{\text{II}}$	$z_{\text{II}}$
K	0	0	0
N	0.5	0	0.486
O	0.445	0.195	0.417

As it will subsequently be necessary to describe the structure in terms of other axial systems, the use of this particular system is denoted by 'm' so that the full symbol for  $a_{\text{II}}$  becomes  $a_{\text{II}}^m$ .

#### Experimental

Suitable crystals were grown by evaporation from ethanol solution: they were very hygroscopic and were mounted in thin walled Pyrex capillaries, sealed with cold-setting 'Araldite'. As an additional precaution against attack by moisture, a small amount of phosphorus pentoxide was included in the capillary. Further details are given elsewhere (Parry *et al.*, 1965).

The cell dimensions were measured on a General Electric Goniostat. In all, the positions of 26 reflexions were measured with Cu  $K\alpha$  radiation and the cell dimensions were extracted using a least-squares routine. The resulting cell dimensions were:  $a_{\text{II}}^m=4.464$ ,  $b_{\text{II}}^m=$

5.007,  $c_{II}^m = 7.383 \text{ \AA}$ ,  $\beta_{II}^m = 116.73^\circ$  and confirm those of Ziegler. Weissenberg photographs taken with Cu  $K\alpha$  radiation confirmed that the only systematic absences were those due to  $C$  face centring and throughout the present work the space group of  $\text{KNO}_2$  II has been taken to be  $Cm$ . All other photographs were taken with Mo  $K$  radiation (unfiltered) using a flat film at distances of between 2.8 and 6.0 cm from the crystal: above room temperature, a microthermostat (Parry *et al.*, 1965) was used to control the crystal temperature.

The principal series of photographs to be discussed in this paper were taken with the crystal oscillating about the axis  $[101]_{II}^m$ .

#### The composite reciprocal lattice of $\text{KNO}_2$ II

The distribution of reciprocal lattice points in the composite reciprocal lattice of a hybrid crystal is controlled both by symmetry elements present only in the point group of the higher symmetry structure (the transformation symmetry) and by the orientation relations which govern the mutual orientation of the two structures. Neither the transformation symmetry  $I \rightarrow II$  nor the mutual orientation of I and II are known in the case of potassium nitrite, but this information can be recovered, in principle at least, from the composite reciprocal lattice by a trial and error procedure.

The guiding rule is that any element of symmetry present in the composite reciprocal lattice of  $\text{KNO}_2$  II that is not present in a single crystal of the same structure must stem from an element of symmetry in  $\text{KNO}_2$  I (*cf.* Parry, 1962). Moreover, such symmetry elements may be detected on the basis of the geometry of the components (split reflexions) alone. Although crystallographically equivalent reflexions in alternative domain orientations may have different intensities for trivial reasons such as the size or frequency of a particular orientation, the splitting of the original single reflexion can occur only if all components are equivalent in the high symmetry structure.

In the present case, oscillation photographs about the axis  $[101]_{II}^m$  of the hybrid crystal showed a horizontal plane of mirror symmetry about the equator which was not present in equivalent photographs of the original crystal. It follows that I must have mirror Laue symmetry in this orientation, and so the axis perpendicular to this mirror plane in I must remain in the same orientation throughout the transformation. If this axis is called  $[010]_I$  then one orientation relation is  $[101]_{II}^m \parallel [010]_I$ .

At an angle of about  $45^\circ$  to  $[010]_{II}^m$ , oscillation photographs of the hybrid crystal II indicated additional elements of symmetry in the composite reciprocal lattice (Fig. 1). There was undoubtedly a vertical mirror plane and its line of intersection with the horizontal mirror plane was taken to define a second axis  $[001]_I$  which must be at least a twofold axis of symmetry. A closer examination of the oscillation photographs suggested that this was actually a fourfold axis and some support for this conclusion was obtained from Laue

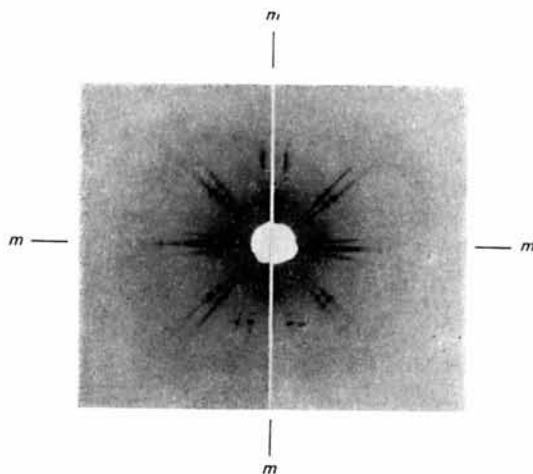


Fig. 1. The development of  $mmm$  symmetry in the composite reciprocal lattice of  $\text{KNO}_2$  II following a thermal cycle through the transformation range of temperature. The illustration shows those parts of two successive oscillation photographs taken about the axis  $[101]_{II}^m$  which lie to the left and right of the main beam respectively (Mo  $K$  radiation). The suspected presence of a fourfold symmetry axis along the main beam direction was disproved by a detailed interpretation of these and similar photographs (see text).

photographs taken near this direction. Provisionally therefore, it was assumed that the symmetry in the direction of  $[001]_I$  was 4 mm and that the high temperature phase of potassium nitrite was either tetragonal or cubic. The unit cell axes of I suggested by these arguments can be derived from those of II as follows:

$$\begin{aligned} a_I &\rightarrow a_{II}^m - b_{II}^m \\ b_I &\rightarrow a_{II}^m + c_{II}^m \\ c_I &\rightarrow a_{II}^m + b_{II}^m \end{aligned}$$

The orientation in the monoclinic lattice of the larger triclinic cell from which this high symmetry form is generated is shown in Fig. 2: with the monoclinic cell dimensions given earlier, these triclinic unit cell dimensions become:

$$\begin{aligned} a_{II} = c_{II}^m &= 6.708 \text{ \AA} & \alpha_{II}^m = \gamma_{II}^m &= 83.47^\circ \\ b_{II}^m &= 6.692 & \beta_{II}^m &= 96.57 \end{aligned}$$

The volume is double that of the conventional cell so that it contains 4 formula units of  $\text{KNO}_2$ . The near equality of the axes of this alternative cell is a consequence of the pseudo-rhombohedral nature of the  $\text{KNO}_2$  lattice discussed later.

Before it is possible to predict  $\xi$  and  $\zeta$  values for the split reflexions from the hybrid crystal II when cubic or tetragonal symmetry is assumed for I, it is necessary to have a second orientation relation between the lattices of I and II. If I is taken to be cubic, with Laue symmetry  $m\bar{3}m$ , then it was assumed that monoclinic symmetry would be preserved in the transformation for the orientation of the monoclinic point group symmetry  $2/m$  is such that it could form a sub-group of  $m\bar{3}m$  (Fig. 3 and *International Tables for X-ray Crys-*

tallography, 1952). The second orientation relation then becomes:

$$(010)_{II}^m \parallel (\bar{1}01)_I. \quad (a)$$

Alternatively, if I is tetragonal with Laue symmetry  $4/mmm$  then the monoclinic symmetry cannot be a subgroup of the transformation symmetry and different orientation relations must arise if the cubic symmetry elements are not to be regenerated. Inspection of the  $hkh$  reciprocal lattice plane suggests two alternative orientations

$$(11\bar{1})_{II}^m \parallel (100)_I \quad (b)$$

or  $(\bar{1}11)_{II}^m \parallel (001)_I. \quad (c)$

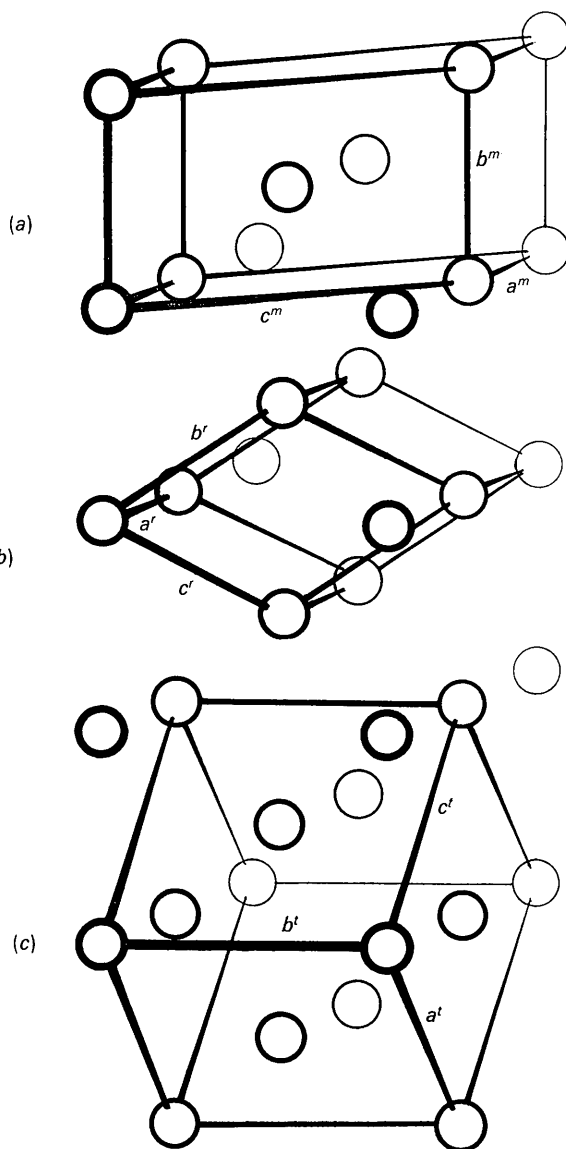


Fig. 2. The orientation of the three axial systems used in the text to describe the space lattice of form II. (a) Monoclinic crystallographic unit cell,  $m$ . (b) Pseudo-rhombohedral unit cell,  $r$ . (c) Triclinic unit cell,  $t$ .

General expressions (in the axial system  $a'_{II}b'_{II}c'_{II}$ ) for the reciprocal lattice vector components of the original crystal of II (the reference domain) resolved along the axes of I, are given below for each of the three possibilities (a), (b) and (c)

$$(a) X = A_1h + B_1k + C_1l$$

$$Y = B_2k$$

$$Z = C_1h + B_1k + A_1l$$

$$\text{with } A_1 = 0.1074, B_1 = -0.0130, C_1 = 0.0069,$$

$$B_2 = 0.1062$$

$$(b) X = A'_1h + B'_1k + C'_1l$$

$$Y = B_2k$$

$$Z = B'_3k + C'_3l$$

$$(c) X = C'_3h + B'_3k$$

$$Y = B_2k$$

$$Z = C'_1h + B'_1k + A'_1l$$

$$\text{with } A'_1 = 0.1076, B'_1 = -0.0138, C'_1 = 0.0139,$$

$$B_2 = 0.1062, B'_3 = -0.0122, C'_3 = 0.1067$$

These expressions for the reference domain can be generalized to include all other domain orientations allowed by the appropriate transformation symmetry (Parry, 1962). The splitting predicted for any reflexion when  $I \rightarrow II$  can then be compared with that observed on the oscillation photographs by using following identities on each domain orientation in turn;  $\xi = (X^2 + Z^2)^{1/2}$ ;  $\zeta = Y$ . To simplify comparison between the three models, attention is focused on the splitting of  $(200)_I$  and  $(202)_I$  which, as  $(k)_I = 0$ , are both associated with the zero layer line of the  $[101]_{II}^m$  oscillation photographs. The  $\xi$ ,  $\zeta$  coordinates predicted in each case are given in Table 1 and shown diagrammatically in Fig. 4. It can be seen that neither  $m\bar{3}m$  nor  $4/mmm$  (at least in the orientation assumed) provides a satisfactory explanation of the observed splitting. Bearing in mind that the magnitude of the coefficients determining the detailed splitting of the reflexions depends on the orientation relations, it is possible to explore the effect of slight changes in the mutual orientation of the two lattices. However, this only serves to con-

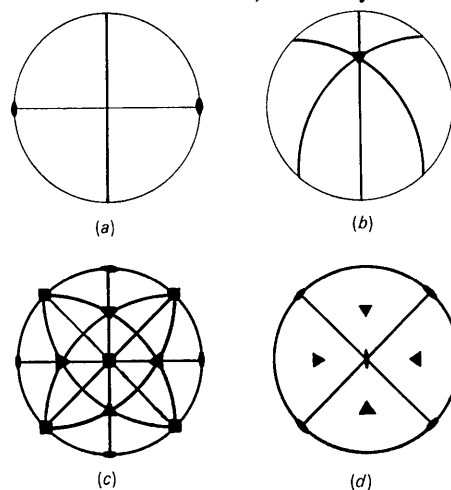


Fig. 3. Stereographic projections of point-group symmetries discussed in the text. (a)  $2/m$ , (b)  $3m$ , (c)  $m\bar{3}m$ , (d)  $m3$ .

firm that neither  $m3m$  nor  $4/mmm$  is an acceptable description of the transformation symmetry.

In the light of this conclusion, it was decided to relax the condition that  $[001]_I$  is a fourfold axis and to consider the various possibilities that arise if the composite reciprocal lattice symmetry in this direction is reduced to  $2mm$ . There are now four possible transformation symmetries:

1. Orthorhombic,  $mm$  or  $mmm$
  2. Tetragonal,  $4/mmm$
  3. Hexagonal,  $6/mmm$
  4. Cubic,  $m3$
- } each with the unique axis  
||  $[010]_I$

The first three symmetries can be rejected without further consideration for they predict that  $\zeta=0$  for all components of the split  $(200)_I$  and  $(202)_I$ . The only

Table 1. Predicted  $\xi$  and  $\zeta$  values from a hybrid crystal of II for different symmetries of I

Reflexion Laue symmetry	Analytical expressions				Numerical values			
	$(200)_I$		$(202)_I$		$(200)_I$		$(202)_I$	
	$\zeta$	$\xi$	$\zeta$	$\xi$	$\zeta$	$\xi$	$\zeta$	$\xi$
$m3m$ (case a)	$\pm 2B_1$	$2(B_2^2 + B_1^2)^{\frac{1}{2}}$	$\pm 2(B_1 + C_1)$	$2[B_2^2 + (A_1 + B_1)^2]^{\frac{1}{2}}$	$\pm 0.026$	0.214	$\pm 0.012$	0.284
	$\pm 2C_1$	$2A_1$	$\pm 2(B_1 - C_1)$	$2[B_2^2 + (A_1 - B_1)^2]^{\frac{1}{2}}$	$\pm 0.014$	0.215	$\pm 0.040$	0.322
	0	$2(A_1^2 + C_1^2)^{\frac{1}{2}}$	0	$[8(A_1 + C_1)^2]^{\frac{1}{2}}$	0	0.215	0	0.323
$4/mmm$ (case b)	$\pm 2B_1'$	$2[B_2^2 + (B_3')^2]^{\frac{1}{2}}$	$\pm 2(B_1' + C_1')$	$2[B_2^2 + (C_3' + B_3')^2]^{\frac{1}{2}}$	$\pm 0.028$	0.214	0.000	0.284
	0	$2A_1'$	$\pm 2(B_1' - C_1')$	$2[B_2^2 + (C_3' - B_3')^2]^{\frac{1}{2}}$	0	0.215	$\pm 0.055$	0.318
			0	$[8(A_1' - C_1')^2]^{\frac{1}{2}}$			0	0.284
$4/mmm$ (case c)	$\pm 2B_3'$	$2[B_2^2 + (B_1')^2]^{\frac{1}{2}}$	$\pm 2B_3'$	$2[B_2^2 + (A_1' + B_1')^2]^{\frac{1}{2}}$	$\pm 0.024$	0.214	$\pm 0.024$	0.283
	0	$2[(C_3')^2 + (C_1')^2]^{\frac{1}{2}}$	$\pm 2B_3'$	$2[B_2^2 + (A_1' - B_1')^2]^{\frac{1}{2}}$	0	0.215	$\pm 0.024$	0.322
			0	$2[(C_3')^2 + (A_1' + C_1')^2]^{\frac{1}{2}}$			0	0.323
$m3$ (case b)	$\pm 2B_3'$	$2[B_2^2 + (B_1')^2]^{\frac{1}{2}}$	$\pm 2(B_1' + C_1')$	$2[B_2^2 + (C_3' + B_3')^2]^{\frac{1}{2}}$	$\pm 0.024$	0.214	0.000	0.284
	$\pm 2C_1'$	$2C_3'$	$\pm 2(B_1' - C_1')$	$2[B_2^2 + (C_3' - B_3')^2]^{\frac{1}{2}}$	$\pm 0.028$	0.213	$\pm 0.055$	0.318
	0	$2A_1'$	$\pm 2B_3'$	$2[B_2^2 + (A_1' + B_1')^2]^{\frac{1}{2}}$	0	0.215	$\pm 0.024$	0.283
$m3$ (case c)	$\pm 2B_1'$	$2[B_2^2 + (B_3')^2]^{\frac{1}{2}}$	$\pm 2(B_1' + C_1')$	$2[B_2^2 + (C_3' + B_3')^2]^{\frac{1}{2}}$	$\pm 0.028$	0.214	0.000	0.284
	0	$2[(C_3')^2 + (C_1')^2]^{\frac{1}{2}}$	$\pm 2(B_1' - C_1')$	$2[B_2^2 + (C_3' - B_3')^2]^{\frac{1}{2}}$	0	0.215	$\pm 0.055$	0.318
	0	$2A_1'$	$\pm 2B_3'$	$2[(A_1' + B_1')^2 + B_2^2]^{\frac{1}{2}}$	0	0.215	$\pm 0.024$	0.283

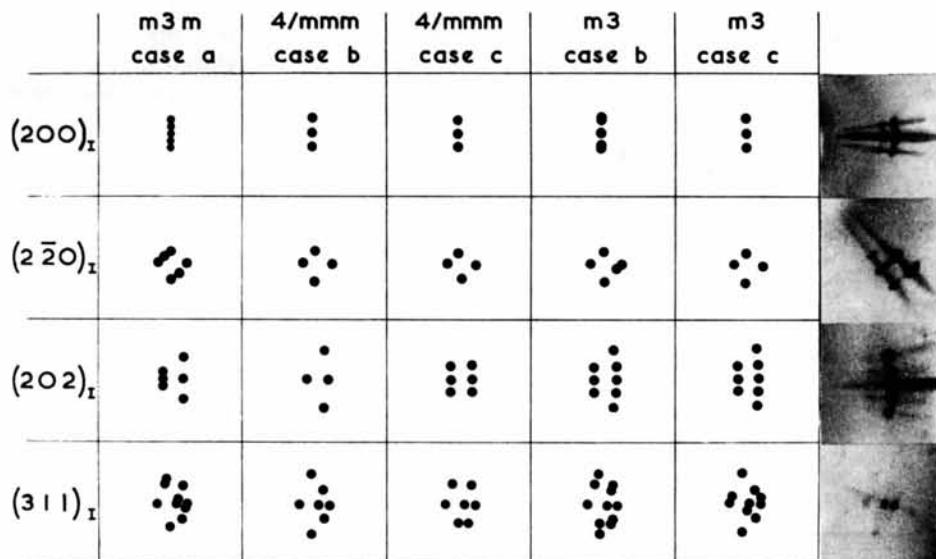


Fig. 4. A comparison of selected 'split' reflexions given by the hybrid crystal of form II with patterns predicted on the basis of various assumed transformation symmetries for the structural change I  $\rightarrow$  II. Particular attention should be paid to the  $(202)_I$  group of reflexions. The observed patterns were recorded with unfiltered Mo K radiation and allowance must be made for the presence of  $K\beta$  reflexions. The indices given relate to those of the corresponding single reflexion in form I.

remaining possibility therefore is that the transformation symmetry is cubic but in the lower symmetry of class  $m\bar{3}$ . The constraint imposed on the orientation relations by virtue of the fact that the monoclinic symmetry elements  $2/m$  are in the correct position to be a sub-group of the cubic symmetry is now removed and the two orientations used earlier for the tetragonal case are again available.

Applying arguments similar to those used above, it is found that these two possible orientation relations cannot be distinguished on the basis of the present diffraction photographs (Fig. 4). However, this is of no consequence, for the two possibilities merely correspond to enantiomorphic representations of the same group. From the reciprocal lattice coordinates in Table 1 and the graphical representations in Fig. 4, it can be seen that both (b) and (c) effectively predict the splittings actually observed. It follows that the transformation symmetry must be  $m\bar{3}$  and therefore that  $\text{KNO}_2$  I is cubic.

It remains to be shown that the orientation relations, which control the number and magnitude of the constants  $A$ ,  $B$ ,  $C$  etc. have also been correctly determined. This requires a quantitative check on the agreement between the observed and calculated  $\xi$ ,  $\zeta$  values. It is difficult to measure these with sufficient accuracy on the existing photographs so that numerical confirmation is not yet possible. Nevertheless, the detailed splitting of any  $(hkl)_f$  reflexion can now be predicted and experience has shown that the geometrical appearance of the predicted group of reflexions is extremely sensitive to the magnitude of these constants. Table 2 lists  $XYZ$  components for each domain orientation in case (c). A comparison between the observed and calculated patterns in the case of  $(311)_f$  and of  $(220)_f$  is shown in Fig. 4; it can be seen that the agreement is reasonable so that the orientation relations given earlier must be essentially correct.

### Discussion

The results of the above analysis indicate that the transformation symmetry is cubic, class  $m\bar{3}$ . Two alternative explanations can be proposed to account for this observation. These are that

- (i) the point group symmetry of I is really  $m\bar{3}$
- (ii) the point group symmetry of I is actually  $m\bar{3}m$  but that a domain texture based on a sub-group of this symmetry is energetically favoured.

Although further discussion of these alternatives is bound to be speculative, its inclusion in the present paper is felt to be justified on the grounds that it emphasizes those aspects of the problem that deserve further study.

### Structural interpretation

The structural change from monoclinic to cubic symmetry during the transformation  $\text{II} \rightarrow \text{I}$  is not so drastic as might at first appear. The crystallographic data for the monoclinic form given earlier indicate pronounced pseudo-rhombohedral lattice symmetry as can easily be seen by referring the structure to the new axes:

$$\begin{aligned} a_{\text{II}}^r &= a_{\text{II}}^m \\ b_{\text{II}}^r &= \frac{1}{2}(b_{\text{II}}^m - c_{\text{II}}^m) \\ c_{\text{II}}^r &= -\frac{1}{2}(b_{\text{II}}^m + c_{\text{II}}^m). \end{aligned}$$

Inserting values of  $a_{\text{II}}^m$ ,  $b_{\text{II}}^m$  and  $c_{\text{II}}^m$  from the present work, these pseudo-rhombohedral axes, shown diagrammatically in Fig. 2(b), become:

$$\begin{aligned} a_{\text{II}}^r &= 4.464 \text{ \AA} & \alpha_{\text{II}}^r &= 68.30^\circ \\ b_{\text{II}}^r = c_{\text{II}}^r &= 4.460 & \beta_{\text{II}}^r = \gamma_{\text{II}}^r &= 68.17^\circ \end{aligned}$$

This cell contains one formula unit of  $\text{KNO}_2$ .

It is found, moreover, that relatively minor changes in the atomic parameters of the nitrite group ( $\sim 0.1 \text{ \AA}$ ) would allow the structure itself to be described in terms of the space group  $R\bar{3}m$ , with the important proviso that only two of the threefold positions  $x^r x^r z^r$  can be occupied by oxygen atoms. For example, the following structural parameters in the space group  $R\bar{3}m$

	$x^r$	$y^r$	$z^r$
K	0	0	0
N	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
O	0.416	0.778	0.416

would transform to:

Table 2. Axial components for each domain orientation when Laue symmetry of I is  $m\bar{3}$

Domain	$hkl$	$S$	$S^{-1}(XYZ)$	$X$	$Y$	$Z$
1	$hkl$	$I$	$XYZ$	$C_3'h + B_3'k$	$B_2k$	$C_1'h + B_1'k + A_1'l$
2	$hkl$	$m_x$	$\bar{X}YZ$	$C_3'h - B_3'k$	$B_2k$	$-C_1'h + B_1'k + A_1'l$
3	$hkl$	$m_y$	$X\bar{Y}Z$	$C_3'h - B_3'k$	$B_2k$	$C_1'h - B_1'k + A_1'l$
4	$hkl$	$m_z$	$XY\bar{Z}$	$C_3'h + B_3'k$	$B_2k$	$-C_1'h - B_1'k + A_1'l$
5	$klh$	$3^1_{xyz}$	$ZXY$	$C_1'k + B_1'l + A_1'h$	$C_3'k + B_3'l$	$B_2l$
6	$klh$	$3^2_{xyz}$	$\bar{Z}X\bar{Y}$	$-C_1'k + B_1'l + A_1'h$	$C_3'k - B_3'l$	$B_2l$
7	$klh$	$3^2_{xyz}$	$Z\bar{X}Y$	$C_1'k - B_1'l + A_1'h$	$C_3'k - B_3'l$	$B_2l$
8	$klh$	$3^2_{xyz}$	$Z\bar{X}\bar{Y}$	$-C_1'k - B_1'l + A_1'h$	$C_3'k + B_3'l$	$B_2l$
9	$lhk$	$3^2_{xyz}$	$YZX$	$B_2h$	$C_1'l + B_1'h + A_1'k$	$C_3'l + B_3'h$
10	$lhk$	$3^1_{xyz}$	$\bar{Y}Z\bar{X}$	$B_2h$	$-C_1'l + B_1'h + A_1'k$	$C_3'l - B_3'h$
11	$lhk$	$3^1_{xyz}$	$Y\bar{Z}X$	$B_2h$	$C_1'l - B_1'h + A_1'k$	$C_3'l - B_3'h$
12	$lhk$	$3^1_{xyz}$	$\bar{Y}Z\bar{X}$	$B_2h$	$-C_1'l - B_1'h + A_1'k$	$C_3'l + B_3'h$

	$x^m$	$y^m$	$z^m$
K	0 (0)	0 (0)	0 (0)
N	$\frac{1}{2}$ ( $\frac{1}{2}$ )	0 (0)	$\frac{1}{2}$ (0.486)
O	0.416 (0.445)	0.181 (0.195)	0.403 (0.417)
'hole'	0.778	0	0.584

in the monoclinic space group  $Cm$ . (The values given in parentheses are Ziegler's final parameters.)

As the scattering from the potassium atoms must dominate the X-ray diffraction intensities, this pseudo-symmetry should be detectable in Ziegler's original data, and Table 3 shows that this is indeed so. Since the structure proposed by Ziegler is only approximate and based solely on a qualitative interpretation of the diffraction data, the presence of this pronounced pseudosymmetry raises the further question of whether the oxygen atoms are ordered as required by the monoclinic space group assigned by Ziegler, or whether they are really disordered so as to raise the symmetry of the structure to rhombohedral. The absence of a threefold axis of structural symmetry in form II was carefully established in the present case by the use of Laue photographs. Although the position of the reflexions conformed to trigonal symmetry, their intensities did not. Therefore the structure must be monoclinic:\* the lack of disorder in the orientation of the nitrite group must be a consequence of a strong interaction between these ions.

\* A recent note (Tanisaki & Ishimatsu, 1965) reports the opposite conclusion based on the preliminary results of a structural study.

Table 3. Pseudo-rhombohedral lattice symmetry of monoclinic potassium nitrite

$(hkl)_{II^m}$	$(hkl)_{II^r}$	$\sin \theta$		Intensity
		Ziegler	Present work	
100	100	0.0879	0.0892	<i>w</i>
011, 0 $\bar{1}$ 1	00 $\bar{1}$ , 0 $\bar{1}$ 0	0.0891	0.0892	<i>w</i>
020	01 $\bar{1}$	0.1423	0.1420	<i>m</i>
111, 1 $\bar{1}$ 1	10 $\bar{1}$ , 1 $\bar{1}$ 0	0.1400	0.1421	<i>m</i>
20 $\bar{2}$	211	0.1578	0.1616	<i>s</i>
11 $\bar{3}$ , 1 $\bar{1}$ $\bar{3}$	121, 112	0.1623	0.1618	<i>s</i>
002	0 $\bar{1}$ $\bar{1}$	0.1070	0.1078	<i>vs</i>
11 $\bar{1}$ , 1 $\bar{1}$ $\bar{1}$	110, 101	0.1083	0.1075	<i>s</i>
102	1 $\bar{1}$ $\bar{1}$	0.1645	0.1676	<i>m</i>
120, 120	11 $\bar{1}$ , 1 $\bar{1}$ 1	0.1672	0.1680	<i>m</i>

In order to discuss the orientational disorder of the nitrite group in I it is convenient to note that in II the nitrite group is coordinated by six potassium ions which lie at the corners of an octahedron. The dimensions of the centrosymmetric coordinating polyhedron are shown in Fig. 5: it can be seen that the effect of the pseudo-rhombohedral lattice geometry is to give the polyhedron the point symmetry  $\bar{3}$ . Thus any atom at the centre of the octahedron will experience a field of this symmetry due to the cations. Although Ziegler's structure suggests that the nitrogen atom of the nitrite group is slightly displaced from this central position by about 0.125 Å, it is apparent that there are six alternative orientations for the nitrite group within the coordinating potassium octahedron which are effectively equivalent and distinguishable mainly by the positions of the oxygen atoms. The single orientation

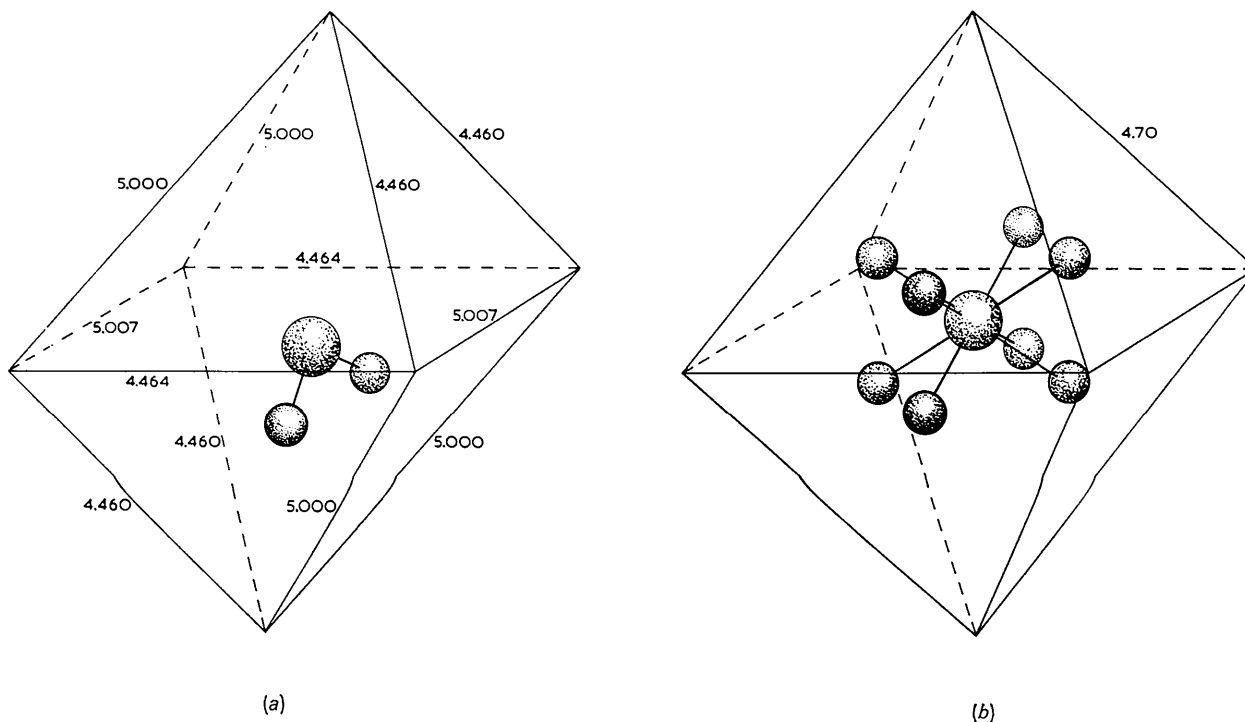


Fig. 5. A comparison of the coordination polyhedra of potassium ions around a nitrate group in (a) form II (monoclinic), (b) form I (cubic). For clarity, drawing (b) has been considerably oversimplified by making the ONO angle equal to the tetrahedral angle.

of the nitrite group found experimentally must imply a strong dipole interaction between the nitrite groups.

When the structure changes from II to I the coordinating polyhedron becomes a regular octahedron and the nitrogen atom may be taken to lie at the centre of the octahedron. The symmetry of the nitrite site is raised to  $m\bar{3}m$ , and the number of possible orientations of the nitrite ion increases to 24. Statistically, therefore, it appears that I should have the rock salt structure and it is unlikely that the lower transformation symmetry  $m\bar{3}$  arises for structural reasons. The estimated dimensions of the octahedron in I, 4.70 Å, is based on the observed volume change of 0.27% at the transition (Hazlewood, Rhodes & Ubelohde, 1963) which predicts a cubic cell parameter of  $a_f = 6.66$  Å.

#### Textural interpretation

As has been suggested previously (Cimino & Parry, 1961), the need to minimize the internal surface energy and the deformation energy of a hybrid crystal may restrict the orientation changes that can occur between a given domain and its neighbours, and could in principle preclude certain domain orientations entirely. If, as suggested above, the symmetry of I is cubic  $m\bar{3}m$  then it follows that the lower transformation symmetry must have arisen for just this reason. As shown below, it is entirely reasonable to suppose that a mechanism exists whereby a crystal of I could transform to domains of II and yet utilize only a sub-group of the structural symmetry of I as elements of interdomain symmetry. It must be pointed out, however, that the group  $m\bar{3}m$  contains two enantiomorphic representations of the group  $m\bar{3}$ , so that the realization of this

lower transformation symmetry throughout an entire crystal implies not only that it is physically possible for domains related by this symmetry to coexist locally within the crystal but also that domains related by the enantiomorphic representation of this group do not arise elsewhere in the crystal during the nucleation of II within I. Studies of the phase change I  $\rightarrow$  II under the polarizing microscope have shown that the change proceeds from a single nucleus at the edge of the crystal, thus satisfying this further condition.

The main point to be established, therefore, is that domains could coexist in the transformation symmetry  $m\bar{3}$ . Using the crystallographic data given earlier (including the estimated cell dimension of I), the equations describing the structural deformation during the transformation I  $\rightarrow$  II, *i.e.* the fractional displacement of atoms in II from their ideal positions in the cubic lattice of I, are:

$$\begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix} = \begin{pmatrix} -0.006 & 0 & 0 \\ 0.115 & 0.008 & 0.115 \\ -0.115 & 0 & 0.001 \end{pmatrix} \begin{pmatrix} u \\ v \\ w \end{pmatrix}$$

where  $uvw$  are the coordinates of a cubic lattice point relative to an arbitrary zero. The large off-diagonal terms in the deformation matrix show that extensive readjustments of atomic positions (presumably by dislocation arrays) must occur even during the single-crystal transformation II  $\rightarrow$  I. Although similar mechanisms must operate during the reverse change, it would be anticipated that such atomic displacements would also be reduced through the selection of appropriate domain orientations.

One simple mechanism would be a twinning mode of II [Fig. 6(a)], in which the twins are related by a twofold axis parallel to  $[010]_{II}$ , *i.e.*  $[101]_{III}$ . As this axis remains parallel to  $[010]_I$  during the transformation, such a twinning mode can function as an element of interdomain symmetry. The composition plane between these twins is  $(101)_{II}$ , *i.e.*  $(10\bar{1})_{III}$ . Repetition of this twinning mode could result in a domain texture with zero macroscopic deformation along the  $x$  and  $z$  axes and with only a small deformation along  $y$ , which is common to both structures. Such a texture [Fig. 6(b)] would account for the long, thin, parallel domains of II observed after the transformation I  $\rightarrow$  II (Parry *et al.*, 1965).

However, the appearance of domains in which the axes  $[101]_{III}$  are oriented along other cube axes implies domains which are related by the threefold axis of cubic symmetry. A stereographic projection of two such domain orientations indicates that they have no common interface: the only common geometrical feature is that the direction  $[10\bar{1}]_{II}$  in one domain is parallel to  $[011]_{II}$  in the other. Because of the geometrical pseudosymmetry of II, these two zones have effectively the same repeat distances, but this coincidence of a single atomic row in the two domains cannot fix the absolute orientation of the second domain because rotation about this axis is still possible.

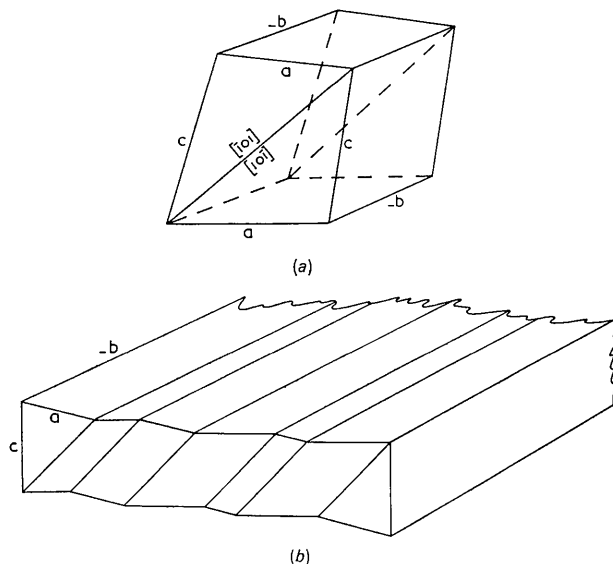


Fig. 6. Proposed twofold rotation twinning mode in the hybrid crystal of form II. (a) Isolated twin. (b) Multiple twin which would account for the observed appearance of a hybrid crystal as reported by Parry *et al.* (1965). The axes relate to the triclinic unit cell of form II; only their respective orientations are indicated in (b).

However, if a domain in the third orientation of the threefold axis is considered, then it is apparent that this can be related both to the second and to the first domain in a similar way, thereby fixing the mutual orientation of all three domains (Fig. 7). This suggests that domains related by the threefold axis ought to arise simultaneously and have a markedly different domain shape from that reported so far. Although this point must receive further study, it is feasible that the crystals selected for study under the microscope might behave differently from the crystal used to obtain the transformation symmetry by diffraction methods. For instance, the shape of the crystal may be important; again, slight traces of water may influence the domain texture, for only in the case of the X-ray measurements were stringent precautions taken to prevent water vapour from reaching the crystal.

However, this is a topic for future research. The point at issue is that there are grounds for believing that both twofold and threefold axes of interdomain symmetry could occur in the transformation  $I \rightarrow II$  and that these two elements of symmetry are sufficient to generate the closed cubic group 23. As the Laue symmetry of such a transformation texture would be  $m\bar{3}$ , it is concluded that the transformation symmetry observed in potassium nitrite does not reflect the full symmetry of the structure of form I but is instead a consequence of the requirement that domains of the form II structure must coexist within the envelope of the initial single crystal. At the present stage of the investigation, this conclusion can only be regarded as a working hypothesis. Nevertheless, it is apparent that the analytical methods discussed in this paper present a powerful means of extracting the maximum amount of information from a limited amount of data and of focusing attention on those crystallographic and solid

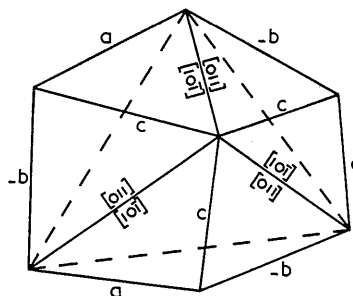


Fig. 7. A possible threefold rotation twinning mode in the hybrid crystal of form II showing how the relative orientation of the three components could be defined by the geometrical equivalence of  $[10\bar{1}]$  and  $[110]$ . The axes relate to the triclinic unit cell of form II.

state aspects of the problem that must receive further investigation.

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