decide which one, if any, of the three fundamental modulations is applicable, before any parameter can be determined from the zeros of the main reflexions and the satellites.

This paper only deals with positional fluctuations of the transverse type. The rules given here are therefore only applicable if the features characteristic for this type of modulation are observed. However, if the structure is affected by density fluctuations or positional fluctuations of the longitudinal type different criteria have to be applied.

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A Probable Crystallographic Path for the Thermal Phase Transitions in Single Crystals of KNO_3

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A probable crystallographic path for the thermal cycle of phase transformations, II–I–III–II, in KNO_3 single crystals is proposed. It is based on the symmetry of the phases and a least-motion hypothesis that the 'shuffles' of the transformations (so remarkably like martensitic transformations in metals) are the minimum possible readjustments subject to accepted van der Waal distances between chemically non-bonded atoms. Twinning is adequately explained by the alternative paths provided by the symmetry of the parent phase. The observed disorientation of 2°9′ in the *c*(II) axes of the end-phase twinned crystals is calculable by the well known Bowles–Mackenzie matrix method. The calculated value is now found to be 2·5°. Crystallographically an important possibility emerges: the structure of the higher-symmetry phase of a transformation may be predicted from only its unit-cell dimensions and space group if the crystal structure of the low-symmetry phase is known.

Introduction

Martensitic transformations in metals and alloys are characterized by well-defined orientation relationships between the parent and product phases. This characteristic is found in phase transformations of crystals of some non-metallic compounds also. For example, calcium carbonate transforms from room-temperature orthorhombic aragonite to rhombohedral calcite at 478 °C. The twofold *c* axis of aragonite becomes the unique axis of calcite (Shoji, 1933).

It has been shown that the reverse transformation, calcite to aragonite, is brought about by shear processes that occur only during crushing and grinding but not by uniform pressure (Leiserowitz, Schmidt & Shamgar, 1962). Shear is also a specific characteristic of martensitic transformations.

At room temperatures phase II KNO_3 crystals are isomorphous with aragonite, space group *Pmcn* (No. 162, *International Tables for X-ray Crystallography*, 1952). On heating they transform at 128 °C to the rhombohedral phase I, space group $R\bar{3}m$ (No. 166). This space group is very close to $R\bar{3}c$ (No. 167) of calcite. X-ray oscillation photographs show that in KNO_3 also the *c* axis of phase II transforms into the unique axis c_H of phase I.

On cooling, phase I KNO_3 returns to phase II not directly but through another rhombohedral phase III of the noncentrosymmetric space group *R*3*m* (No. 160). The transformation sets in at 125 °C, and phase III persists till 110 °C.

The crystal structures of all three phases have been determined (Tahvonen, 1949; Edwards, 1931; Barth, 1939). Their crystallographic data are in Table 1; the three structures in their respective (001) projections are shown in Figs. 1 and 2.

Such closely related symmetry, the similar orientation relationships and the fact that in one of them

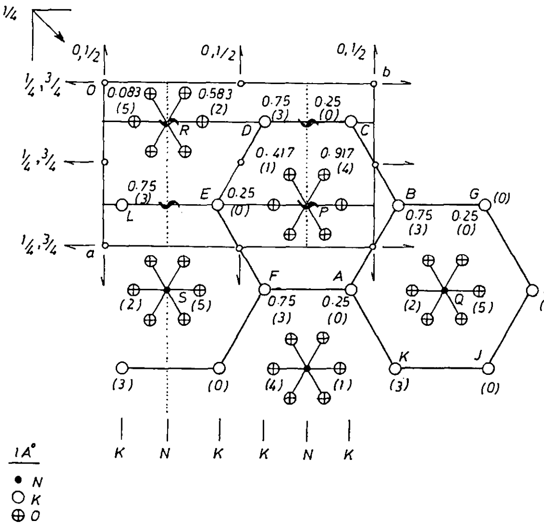

Fig. 1. Phase II structure in (001) projection. z coordinates of ionic centres, N and K, marked. The levels of ionic centres in units of separation are in parantheses. The KNK... sandwich arrangement of layers along the **b** is shown. The NKN... sandwich arrangement along **c** may be seen in the level numbers. [See also Fig. 4(*a*)].

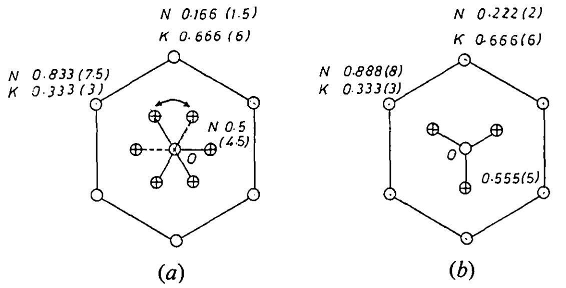

Fig. 2. Structure in (001) projection: (*a*) phase I, (*b*) phase III. The double-headed bent arrow is to show that the anion in phase I has at least a hindered oscillation of 60° amplitude. Phase I has an average centre of symmetry. Both structures may be completely reconstructed in terms of minimum rhombohedral symmetry [See Fig. 3(*b*)].

(calcite) shear processes are involved make it tempting to suppose that the orthorhombic–rhombohedral transformations in $CaCO_3$ and KNO_3 crystals are also martensitic in nature.

Generally, martensitic transitions involve lattice shear deformations leading sometimes to macroscopic shape change in the crystals that transform from one phase to another. The symmetry of the atomic arrangements may not be the same in the two, and then the lattice deformation is accompanied by 'shuffles', *i.e.* atoms and atomic groups move to new positions and take up new orientations to produce the required symmetry of the daughter phase from the old symmetry of the parent phase (Christian, 1965). We discuss here the lattice deformations and shuffles in the thermal cycle of phase transformations in single crystals of potassium nitrate.

1. Lattice deformation

The orthohexagonal (primed) and hexagonal coordinate axes of a rhombohedral lattice are related by (see Fig. 3):

$$\mathbf{a}'=\mathbf{a}_H(1),\quad \mathbf{b}'=\mathbf{a}_H(1)+\mathbf{a}_H(2),\quad \mathbf{c}'=\mathbf{c}_H;$$
$$b'/a'=\sqrt{3}.$$

The coordinate axes of phase II KNO_3 are respectively parallel to the orthohexagonal axes of the rhombohedral phases I and III. The lattice parameters of phases I and III (Fischmeister, 1956) are in Table 2. The phase II cell dimensions extrapolated to 110°C (temperature of the transition III → II) and 128°C (temperature of the II → I transition) according to thermal expansion data (Lonappan, 1956) are also given. Even after extrapolation the ratio b/a in phase II is different from $\sqrt{3}$, the value it must have for rhombohedral symmetry. There is thus lattice deformation when transformations take place. In the II → I transformation the Bain distortion (referred to phase II) is $({}_{\rm II}B_{\rm II})=0{\cdot}99941/1{\cdot}02250/0{\cdot}98122$, and in the III → II transformation it is $({}_{\rm III}B_{\rm III})=0{\cdot}99899/0{\cdot}97681/1{\cdot}07811$ (referred to phase III).

Table 1. *Unit-cell data on phases* I, II *and* III *of* KNO_3

Phase	Temperature of measurement	Unit-cell data a b c	Reference
II	19°C	5·414 9·164 6·431 Orthorhombic $Pmcn$ $Z=4$	Swanson, Fuyat & Ugrinic (1954)
I	128°C	5·423 5·423 9·638 Hexagonal $Z=3$ 4·49, $\alpha_R=73°50'$ Rhombohedral $R\bar{3}m$ $Z=1$	Fischmeister (1956)
III	110°C	5·430 5·430 9·095 Hexagonal $Z=3$ 4·37, $\alpha_R=76°56'$ Rhombohedral $R3m$ $Z=1$	Fischmeister (1956)

Table 2. *Orthogonal cell parameters of the three phases*

Phase	Temperature measured	Temperature extrapolated	Unit-cell data *a*	*b*	*c*
II	19°C		5·414	9·164	6·431
		110°C	5·425	9·183	6·438
		128°C	5·426	9·186	6·549
I	128°C		5·423	9·393	9·638
III	110°C		5·430	9·407	9·095

2. Shuffles (displacements and reorientations)

A brief description of the structures of the three phases is given here. It is useful in working out the necessary shuffles from the symmetry of the phases of a transformation.

With the *c* axis vertical, phase II KNO_3 may be visualized as a vertical stack of NKNNKN... sandwiches [see Figs. 1 and 4(*a*)]. K stands here for a plane of the geometric centres of the K^+ ions. N similarly stands for the geometric centres of the anions. The vertical separation from one layer to the next is constant. We may then number the layer levels serially, starting at the K layer at $z=0{\cdot}25$ arbitrarily as the zeroth reference layer. Six times the separation is equal to the *c* axis of phase II. The interlayer separation may be used with advantage as a unit. The K layers are at levels 0,3,6,9,12,15,18,.... There is a set of N layers with the same orientation of the anions at the levels 1,5,7,11,13,17,..., and another with N layers at levels 2,4,8,10,14,16,... in which the orientation of the anions is staggered relative to that of the anions of the first set.

One can also consider phase II KNO_3 as consisting of vertical K and N layers stacked horizontally along the *b* axis as KNKKNK... sandwiches.

Phase I has a vertical, alternating sequence of equidistant K and N layers, one layer separated from the next by 1·5 units along c_H. As in phase I, there is a vertical alternating sequence of K and N layers in phase III also. The K layers are equidistant with a separation (from one K layer to the next) only a little smaller than in phase I. The N layers form an interleaved set of equidistant layers with the same separation. An N layer lies closer to one of the two K layers between which it lies.

Any layer of the vertical stacking is either pure K or pure N in all three phases. But only the horizontal stack of phase II consists of pure K and pure N layers. The layers are mixed in the horizontal stacking of phases I and III.

It is postulated here that the shuffles are least-motion processes, *i.e.* the transformations in the solid state take place by minimal readjustments subject however to accepted contact distances between nonbonded atoms.

2 (i) *Phase* II → *phase* I *transformation*

*R*3 is the minimum rhombohedral symmetry. In the rhombohedral system the lattice points project down the unique threefold axis at the corners and centres of a honeycomb of hexagons. Threefold rotation axes pass vertically through the lattice points. At the centroids of the six triangles of any hexagon of the projection there are alternately 3_1 and 3_2 vertical screw axes characteristic of rhombohedral symmetry [see Fig. 3(*b*)].

In the honeycomb of hexagons of the (001) projection of phase II consider one, *ABCDEF*, formed by the centres of six cations (see Fig. 1). In three dimensions the K's are related by almost perfect threefold symmetry. This is not so, however, for the N's. The threefold symmetry seen in the projection is spurious, for the N's related in projection by apparent pseudo-threefold symmetry are not at the same level, but at different levels: *e.g.* in Fig. 1 there are at *R* and *S* anions at level 2, but at *P* there is no anion at level 2.

Neither the K's nor the N's have 3_1 and 3_2 screw symmetry. To bring about these axes (characteristic of rhombohedral lattices) the following shuffles are needed. First, a shuffle vertically of all the N layers in the horizontal stack, and secondly, a shuffle horizontally of selected K and N layers of the vertical stack. These two are called step I and step II.

Step I is necessary to produce basic threefold rotation symmetry which is present for the K's but absent for the N's in phase II. Threefold rotation symmetry may be obtained if (*a*) the N's at levels 1,4,7,10,13, 16,... are all shifted up by one unit along the *c* axis; or (*b*) the N's at levels 2,5,8,11,14,17,... shift one level down; or (*c*) the first set moves up and the second down, both by half a unit. The two sets of layers are equivalent by phase II symmetry. The last alternative

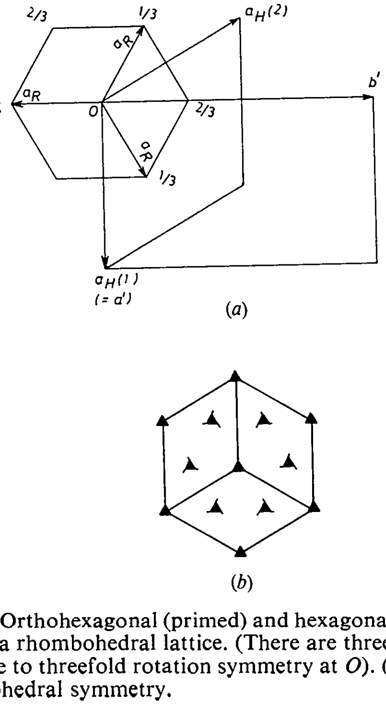

Fig. 3. (*a*) Orthohexagonal (primed) and hexagonal coordinates axes of a rhombohedral lattice. (There are three such sets of axes due to threefold rotation symmetry at *O*). (*b*) Minimum rhombohedral symmetry.

which makes no distinction between them seems the most reasonable, and is what obtains in phase I. In the horizontal stack of KNK... sandwiches step I is that all N layers are displaced, each in its own plane by half a unit along the *c* axis. One set in alternate sandwiches (the first set above) moves up, the other down; the K layers are undisturbed in this step. As a result, the vertical stacking pattern changes to an alternating sequence of equidistant K and N layers with a separation of 1·5 units [Fig. 4(*a*,*b*)].

In this alternating sequence step II is required to bring about 3_1 and 3_2 symmetry. The necessary shuffles are easily found by considering a triangle like *APB* in Fig. 1. In the projection K's and N's must be at all the vertices of the triangle. They must in three dimensions be at proper levels to produce a 3_1 (or 3_2) screw axis at the centroid of the triangle. A displacement *EP*, length equal to the side of the hexagons in projection, will bring a K^+ ion from *E* to *P*. All other necessary shuffles are easily worked out. With displacements along the +ve or −ve directions of the *b* axis denoted by '+' and '−', a rhombohedral arrangement of the representative points of the anions, the N's, is obtained by the following shuffles: N(1·5) +, N(7·5) −, N(10·5) +, N(16·5) −. The number in parantheses denotes the level of the layer involved. Similarly K(0=18) +, K(3) +, K(6) −, K(9) −, lead to a rhombohedral arrangement for the K's. The displacements in all the shuffles are equal to 3·1 Å parallel to the *b* axis, each horizontally in the proper level of a layer involved.

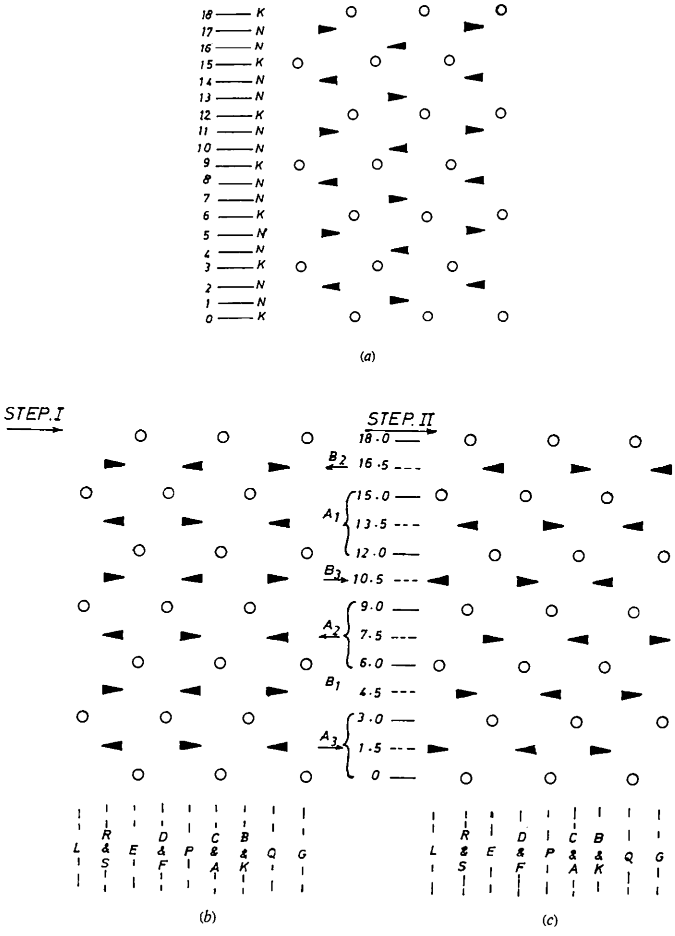

Fig. 4. (*a*) NKN... sandwich stacking along the *c* axis. (*b*) Step I equalizes all pairs of contiguous N levels. Stacking arrangement changes to an alternating sequence of K and N layers. (*c*) Step II produces rhombohedral symmetry but only for the aggregate of representative points. All three arrangements are projected down the *a* (or *a′*) axis. Shaded triangles represent the anions with phase II orientations with one N–O bond along the *b* axis pointing one way or the other. The grouping of layers into *A* and *B* slices is also shown and the directions of their respective step II shuffles by arrows. Note that the periodicity of arrangement along the vertical in (*c*) is 18 units.

The structure at the end of step II has a vertical translation period of 18 units with 12 alternating K and N layers [Fig. 4(*c*)]. We may divide or group the twelve layers as follows:

$$(A_3/B_1/A_2/B_3/A_1/B_2) = \{[K(0), N(1{\cdot}5), K(3)]/N(4{\cdot}5)/ \\ [K(6), N(7{\cdot}5), K(9)]/N(10{\cdot}5)/ \\ [K(12), N(13{\cdot}5), K(15)]/N(16{\cdot}5)\}.$$

Step II shuffling may then be described thus: $A_2(-)$ and $A_3(+)$ shuffle in opposite directions across stationary B_1, and $B_2(-)$ and $B_3(+)$ across stationary A_1 [Fig. 4(*b*)].

It may be pointed out here that step II shuffles can take place in a slab 18 units thick from K(3) to N(19·5). The division into slices $(A_3/B_1/A_2/B_3/A_1/B_2)$ starting from K(3) is again (KNK/N/KNK/N/KNK/N). The shuffles necessary are $A_2(+)$ and $A_3(-)$ across stationary B_1, and $B_2(+)$ and $B_3(-)$ across stationary A_1. The 3_1 and 3_2 screw axes of symmetry change places.

2 (ii) *Reorientation of the anions*

The two steps described above lead to rhombohedral symmetry $R\bar{3}m$ only for the aggregate of the representative points K and N. Rhombohedral symmetry is lost when the points N are replaced by the anions that they represent with their respective phase II orientations [see Fig. 5(*a*,*b*)]. For threefold rotation symmetry at *P*, the anions at level 1·5 at the points *D*, *B* and *F* (for example) must have the same orientation, but the orientation at *B* is not compatible with that at *D* and *F* for threefold rotation symmetry. Suitable reorientation of the anions becomes necessary. A symmetry argument for the necessity of reorientation may be given. In phase II an anion has in a plane parallel to its own, three K^+ ions as nearest neighbours at the corners of an equilateral triangle. Three more cations on the other side complete an octahedron, but the anion is closer to one triangle which thus determines the anion's orientation. After step II the anion is exactly midway between the two cation triangles. There can be no reason why the anion should be in different orientations relative to the nearest-neighbour cations at levels 1·5 units above and below. An orientation of the anion which is the same relative to both can be achieved if it rotates in its own plane about its own symmetry axis by 30° one way or the other.

Suppose at *P* [Fig. 5(*b*)] the anion at level 4·5 turns by 30° in the anticlockwise sense. Two possibilities arise:

(1) the NO_3^- ion at level 13·5 at *P* also rotates anticlockwise. The anions at *P* at the two levels are still staggered in orientation relative to each other. The smallest c_H translation may then be only 18 units. The 3_1 screw can then have a minimum translation component of 6 units parallel to c_H. The unit-cell translation vectors of the rhombohedral lattice will be *PB*, *PD* and *PF* which may be used to determine the reorientation of every other anion. The reorientations fall into a neat cooperative pattern. The centres of the anions lie [Fig. 5(*b*)] on a set of parallel, equidistant vertical planes perpendicular to the *a* axis and with a separation of *a*/2. All anions with centres on the same plane reorient themselves in the same sense. The sense of rotation alternates from one plane to the next as shown. The result of this pattern of reorientation is seen in Fig. 5(*c*). The symmetry of the arrangement is $R\bar{3}c$ which is also the symmetry of calcite and sodium nitrate.

(2) If the NO_3^- ions at levels 4·5 and 13·5 at *P* [Fig. 5(*b*)] turn in opposite senses they come into the eclipsed configuration. c_H can now be only nine units; the translation component of the 3_1 screw axis will be only three units parallel to $\mathbf{c}_H$; the rhombohedral unit-cell translations will be *PA*, *PC* and *PE*. The reorientations do not fall into a neat simple pattern as in the other case. The resultant structure (Fig. 6) has the symmetry *R*32 (No. 155).

2 (iii) *Free of hindered rotation of the anions in* KNO_3 *phase* I

Neither possibility yields $R\bar{3}m$, the symmetry of phase I. This required symmetry will result from both $R\bar{3}c$ and *R*32 if the anions rotate freely in their own planes, or make hindered oscillations with an amplitude of 60°. The effective time-averaged symmetry will be $R\bar{3}m$. The c_H translation of 18 units in the first possibility above will also be halved to nine units. The rotation and vibration of the anions in phase I has already been argued from X-ray analysis (Tahvonen, 1949).

2 (iv). In the discussion of the transformation so far the anion has been implicitly treated as a rigid group of atoms. The nitrate ion is stable even in melts. Dissociation entropy of the nitrate ion is 25 e.u., much higher than the fusion entropy of 5 e.u. in alkali and ammonium nitrates (Ubbelohde, 1965). Spectroscopic evidence from fused nitrates points only to a degradation of the symmetry of an NO_3^- ion from D_{3h} to C_{2v} with a maximum angle distortion of 10° and an N–O bond perhaps 0·15 Å longer than the others. Self-diffusion coefficients (Dworkin, Escue & Artsdalen, 1960) and transport number (Labrie & Lamb, 1963) have been reported for the ion in studies on molten salts. The fusion temperature of potassium nitrate is 338°C. The assumption of a rigid anion at temperatures below 130°C may be considered justified.

3. Phase I → phase III transformation

Only a centre of inversion is lost in this transformation from $R\bar{3}m$ symmetry to *R*3*m*. It is easily lost if the rotating anions of phase I merely stop rotating or oscillating with 60° amplitude. For *R*3*m* symmetry and c_H = nine units the anions must lie in the same orientation relative to the N–O bonds on the mirror planes. Such an orientation at the body centre is unlikely [as already mentioned in § 2(ii) when the necessity for reorientation was argued]. The anions move away from the body centre along $\mathbf{c}_H$ and are locked into orientations dictated by the nearest three cations. The off-centre displacement may take place along either direction. If the displacements in neigh-

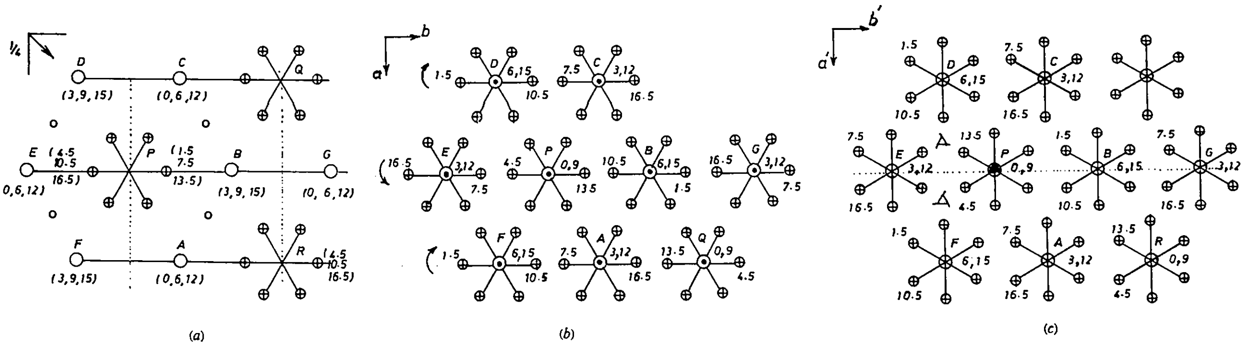

Fig. 5. (*a*) *c*-axis projection of phase II. (*b*) The ionic arrangement and orientations [preserved from phase II in (*a*)] after the linear displacements of steps I and II. Note that the anions' orientations are incompatible with threefold symmetry. Bent arrows in (*b*) denote the reorientations necessary by rotation through 30° of all anions in the sense of the arrow at the left of each row. The resulting structure (*c*) has c_H = 18 units and symmetry $R\bar{3}c$.

bouring cells are correlated phase III should consist of domains of positive and negative polarization. It has been found (Shinnaka, 1962) that at 125°C the anions in phase I take up the premonitory orientations and are displaced from the body centres. Phase III is polar and ferroelectric, and a coercive field along $\mathbf{c}_H$ is known to change the sign of polarization of the domains (Sawada, Nomura & Asao, 1961).

The displacement off-centre is not limited by considerations of symmetry. But contact distances between non-bonded atoms are known to vary only in a very narrow range (Kitaigorodskii, 1955). If the K–O distance in phase II with non-rotating nitrate ions is accepted as average, the displacement of the anion approximately 0·5 Å from the body centre in phase III is only predictable.

The significant shortening of the c_H translation in phase III has been attributed (Gay, 1968) to instability against some lattice vibration modes. These considerations are outside the scope of the present study, which is only on symmetry.

4. Phase III → phase II transformation

It is possible to imagine that on cooling from phase III the transformation passes through an incipient phase I and regains phase II by exactly retracing the path of the II → I → III transformation. There is however no evidence for this. It will also conflict with the least-motion hypothesis.

The path of the III → II transition would be as follows: Consider a phase III domain in which an anion is displaced above the body centre. This would be a domain of negative polarization. In phase III the anions in a domain are all of the same eclipsed orientation. If we consider the vertical stack, the layers are pure K and pure N. But in the horizontal stack the layers in phase III are mixed, unlike in phase II. An exact reversal of step II will separate the K's and N's into a horizontal stack of unmixed K and N layers, in the form of KNK... sandwiches. The anions are at levels 2, 5, 8, 11, ... in the vertical stack. (In a domain of positive polarization they would be at levels 1, 4, 7, 10, ...) The shuffles of N layers in the horizontal stack in only alternate KNK sandwiches one unit down in the domain of negative polarization (up in a domain of opposite polarization) will lead to phase II. As the anion moves closer to the other three nearest-neighbour K^+ ions their orientation changes to the opposite to give the correct level ordering and orientation of ions in phase II. It is assumed that the abnormal c_H contraction of phase III will be restored.

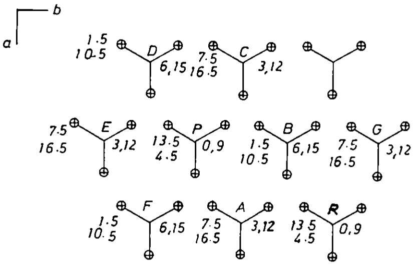

Fig. 6. Rotation of anions to eclipsed orientation will produce a rhombohedral structure of c_H = nine units but symmetry $R32$. The reorientations do not fall into a neat cooperative pattern as in Fig. 5.

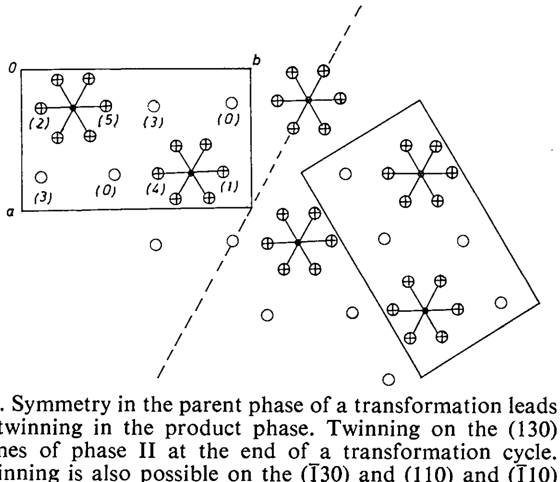

Fig. 7. Symmetry in the parent phase of a transformation leads to twinning in the product phase. Twinning on the (130) planes of phase II at the end of a transformation cycle. Twinning is also possible on the ($\bar{1}$30) and (110) and ($\bar{1}$10) planes of the end phase.

5. Twinning

Twinning is to be expected when by reason of symmetry of the parent phase alternative and equivalent paths are available for a transformation. This leads to crystals of the product phase in different relative orientations.

It has been observed (Kennedy, Ubbelohde & Woodward, 1953) that after a cycle of transformations II → I → III → II the end-phase crystals of potassium nitrate with nearly the same direction of the c axis were turned about this direction by 120° relative to each other. The disorientation of the c axes of the end-phase crystals was measured to be approximately 2°9′. Twinning was observed on the (130) planes and sometimes also on the (110) planes. Twinning on the (110) planes is also known in aragonite (Bragg, 1955). These observations may be readily explained.

The line along which the step II shuffles have been considered so far is parallel to the b axis of the phase II crystal at the beginning. This changes to the b' (orthohexagonal) axis in phases I and III. The reverse shuffles take place parallel to $\mathbf{b}'$, of which in phase III there are now three, completely equivalent to one another. If the shuffles parallel to $\mathbf{b}'$ for step II in reverse occur in adjacent parts of a domain in the same slab, *e.g.* K(0) to N(16 or 17) along two different of the three equivalent b' directions, twinning must occur on the (130) and ($\bar{1}$30) planes of phase II. The lattice deformation and the strain that results from twinning account for the slight observed misalignment of the end-phase crystals. The extent of disorientation may be calculated by the matrix method well known in the crystallographic theory of martensitic transformations in metals (Bowles & Mackenzie, 1962; Wayman, 1964). The calculated value is 2° 30′ in excellent agreement with the observed value.

If the step II shuffles in the II → I transformation occur in the slab K(0) to N(16·5), and the reverse shuffles in the III → II transformation take place in the slab K(3) to N(20) [or N(19)], twinning must occur on the (110) or ($\bar{1}$10) planes. Twinning on the (130) plane is shown in Fig. 7.

6. Conclusion

In this study martensitic-transformation concepts have been applied with success to the thermal phase transformations in calcium carbonate and potassium nitrate. The probable crystallographic paths have been worked out by shuffles assumed to be least-motion processes. The step II shuffles along **b**′ in the III → II transformation bear a strong resemblance to the h.c.p.-to-f.c.c. transformation in cobalt. Many inorganic crystals have been reported in recent years to exhibit characteristics of martensitic transformations. The NaCl type to CsCl type transformations in alkali and ammonium halide crystals have been explained along these lines (Fraser & Kennedy, 1974).

Twinning is adequately explained by the symmetry of the parent phase of the transformation, and the shuffles and reorientations of the ions. Some similarity may be noticed to the ‘Y’ mechanism of mechanical twinning in which the ‘motif’ rotates through a suitable angle about an axis through its centroid (Jaswon & Dove, 1960).

The determination of the habit planes of the transformations of the substances should be useful for a fuller study with martensitic theory.

Crystallographically the following important possibility also emerges. If the crystal structure of the lower-symmetry phase is known, the crystal structure of the higher-symmetry phase may be predicted from a knowledge of only the unit cell and space group of the higher-symmetry phase. This has been verified quite successfully in the phase transformations V → IV → II of ammonium nitrate (Swaminathan, 1975).

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