

Table 4. *Theoretical values adopted for F_g^i*

$F_{220}^i(\text{PH})^{(a)}$	= 0.340 (\perp polarization)
	= 0.339 (\parallel polarization)
$F_{440}^i(\text{PH})^{(a)}$	= 0.309 (\perp polarization)
	= 0.302 (\parallel polarization)
$F_{220}^i(\text{CO})^{(b,c)}$	= 0.009
$F_{440}^i(\text{CO})^{(b,c)}$	= 0.004
$F_{220}^i(\text{TDS})^{(b,c)}$	= 0.007
$F_{440}^i(\text{TDS})^{(d)}$	= 0.007

(a) Hildebrandt, Stephenson & Wagenfeld (1975). (b) Sano, Ohtaka & Ohtsuki (1969). (c) Giardina & Merlini (1973). (d) Tentatively assumed.

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Orientations and Twinning in the Structural Transformation Aragonite-type to Calcite-like in Potassium Nitrate Crystals

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The structural transformation $\text{KNO}_3 \text{ II} \xrightarrow{128^\circ\text{C}} \text{I}$ was studied by X-ray diffraction and microscopy. Orientations measured by diffraction were (a) $[10\bar{1}]_I \parallel [010]_{II}$, $(110)_I \parallel (001)_{II}$ and (b) $[01\bar{1}]_I \parallel [010]_{II}$, $(11\bar{1})_I \parallel (100)_{II}$ (rhombohedral indices, $Z=4$ for I). Two orientations measured by optical and surface analysis agree with two previously found for CaCO_3 in glaucophane schists. Transformed specimens recrystallized at 180°C . There is some optical evidence for twinning. The symmetry options of relation (b) would allow $(110)_I$ transformation twinning which could simulate mechanical twinning. The possibility of crystallographically controlled mechanisms is discussed.

The transformation of the aragonite to the calcite structure is of interest both for its possible combination of reconstructive and shear-like components in the mechanism of this change of first coordination, and as an indicator in low-grade metamorphism in rocks. This structure change is well known in calcium carbonate: a very similar transformation occurs in potassium nitrate, KNO_3 . Below 128°C potassium nitrate has a closely pseudo-hexagonal aragonite structure (II), space group $Pm\bar{c}n$, $Z=4$ (Edwards, 1931; Nimmo &

Lucas, 1973), and at higher temperatures the high- NaNO_3 structure (I), space group $R\bar{3}m$, in which there is considerable thermal oscillation of the NO_3^- ions (Shinnaka, 1962; Strømme, 1969). Though this differs from calcite in the relative mean orientations of the anions the difference must become less significant at higher temperatures because of the increased amplitude of oscillation of the CO_3^{2-} ions. The morphological subcell of calcite is a true cell of KNO_3 I, which grows with similar rhombohedral morphology (Kennedy, 1972). This cell has $Z=4$, $a=7.04 \text{ \AA}$, $\alpha=100.8^\circ$. The volume change in KNO_3 is 0.7%.

In the aragonite structure the cations are arranged

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almost as in hexagonal close packing, whereas in the calcite structure the cation array is as in cubic close packing uniformly expanded normal to the threefold axis. It has therefore been suggested that during transformation the basal layers translate to alter the stacking sequence (Shoji, 1933; Kôzu & Kani, 1934). The resulting orientation relation (*A*) would be $[111]_I || [001]_{II}, (1\bar{1}0)_I || (100)_{II}$. Kennedy & Odlyha (1974) pointed out that this relation would require martensitic accommodation of misregistry at an $(001)_{II}$ interface, but commented that the reasonably good match between the planes $(001)_{II}$ and $(111)_I$ was not necessarily sufficient to determine the choice of mechanism. Swaminathan & Srinivasan (1975) described the displacements and the martensite geometry for relation *A* in the reverse transformation $I \rightarrow II$ using the transformation twinning of *II* (Kennedy, Ubbelohde & Woodward, 1953) as the lattice-invariant shear. Kennedy & Kriven (1972) concluded from surface effects that shear components operated in the mechanisms of transformation $II \rightarrow I$ even when relation *A* did not apply. Buerger (1951) classified the transformation as typically reconstructive, mainly because of the difference of coordination of the cations by oxygen in the fully ordered structures. Relation *A* has been observed in CaCO_3 by Hiragi, Kachi, Takada & Nakanishi (1966) by electron diffraction. X-ray diffraction showed the orientation $[111]_I || [001]_{II}, (1\bar{1}0)_I || (010)_{II}$ (relation *B*) in KNO_3 (Kennedy & Kriven, 1972) and in CaCO_3 (Das Gupta, 1964). In this relation the product orientation is rotated 90° around $[001]_{II}$ from *A*. In X-ray diffraction studies of KNO_3 , Davis & Oshier (1967) (DO) found only a different orientation, $(101)_I || (001)_{II}, [10\bar{1}]_I || [010]_{II}$. Brown, Fyfe & Turner (1962) (BFT) investigated calcium carbonate from glaucophane schists by means of light microscopy and found several other orientation relations, including $(101)_I || (010)_{II}, [10\bar{1}]_I || [100]_{II}$ (BFT I) and $(010)_I || (001)_{II}, [10\bar{1}]_I || [100]_{II}$ (BFT II). These authors discussed their results in relation to thermal transformation, but DO considered that the BFT relations were due to hydrothermal replacement. The possibility of twinning in the transformation $II \rightarrow I$, when the basal planes do not persist, was indicated by the surface traces (Kennedy & Kriven, 1972) but otherwise appears not to have been discussed. Normal crystals of aragonite, naturally occurring in strained marble, were observed to coexist intimately with twinned calcite, where calcite was the stable phase, and were thought to have grown metastably by direct transformation from the calcite, because of the stored strain energy due to mechanical twinning (Newton, Goldsmith & Smith, 1969). Evidently the transformation is neither simple nor fully understood. In the present work the transformation KNO_3 $II \rightarrow I$ in single crystals has been investigated by optical and X-ray methods. The results show that orientations in which the basal plane $(001)_{II}$ does not become $(111)_I$ are common, and that transformation twinning is possible.

Experimental

The starting material was analytical grade KNO_3 twice recrystallized from conductivity water. For microscopy, batches of elongated crystals lying on $(010)_{II}$, about 0.1 mm wide and 0.01 mm thick were grown from aqueous solution on glass cover slips, vacuum dried, and examined on a large polarizing microscope fitted with a transparent heater at magnifications up to 600. Microscopy readily shows whether the basal planes $(111)_I, (001)_{II}$ are not parallel, since their persistence, as in relations *A* and *B*, requires the fast extinction direction to be maintained through the transformation. When some transformed crystals were further heated to 150°C and rapidly cooled, but not transformed back to phase *II*, they mechanically twinned. By measuring both the fast extinction direction, and the angles of the twin traces on adjacent faces, which are at 60° to (010) , it was possible to carry out two-surface analyses and determine the orientation in these annealed crystals, with methods given by Barrett (1952) and Bevis, Heckscher & Crocker (1964).

For X-ray diffraction individual dried crystals (0.3 mm wide) were attached by a smear of high-temperature silicone grease to a thin glass heater carried on the goniometer head. For each specimen an individual product grain was aligned in the X-ray beam by means of a polarizing microscope attached to the X-ray camera. Laue and precession photographs were taken with Mo radiation. All orientations are subject to an uncertainty of $\pm 3^\circ$ due to stereographic manipulations and some change of shape of the crystal.

Results

On the microscope, many crystals could be transformed with slow movement of an interface 3° from $(001)_{II}$. These developed tilted steps parallel to the interface (Odlyha, 1970). The regular tilts imply a shear component in the mechanism. In some of these crystals the original extinction direction was maintained within 5° . In others most of the new extinction directions were in the ranges $16 \pm 3^\circ$ and $27 \pm 3^\circ$, but in some blocks the fast extinction direction rotated 85° around $[010]_{II}$ or 90° around $[100]_{II}$. In the usual orientation of the original crystals on the stage, the DO relation would result in an extinction direction of 27° as observed. The angle of 16° is similarly consistent with a pseudo-symmetry option of this relation (owing to the pseudo-symmetry of *II*), and suggests that pseudo-options exist. It was evident from these optical measurements that the basal planes did not always persist, and that there were orientations which had not previously been recognised.

Many other crystals however superheated up to 15°C . Each ultimately transformed suddenly throughout. These showed no detectable surface effects. There was no evidence for the $(001)_{II}$ interface. The extinction was diffuse, a band similar to a compensation band

moving across the crystal as it was rotated between crossed polars. Several crystals in which the extinction became diffuse transformed slowly enough to allow observation of the transformation front. It consisted of narrow parallel spikes which were the tips of lamellae lying at an angle of 24° to $[001]_{II}$ as seen on the $(010)_{II}$ face. These spikes and the diffuse extinction suggest the presence of either twins or martensitically formed lamellae immediately after transformation.

The orientation relations which were deduced from surface analysis in annealed crystals containing only one or two product grains were (1) $(101)_I || (010)_{II}$, $[10\bar{1}]_I || [100]_{II}$ and (2) $\angle (010)_I (001)_{II} = 8^\circ$, $[101]_I || [010]_{II}$, $(3\bar{1}\bar{1})_I || (\bar{1}10)_{II}$.

The relations measured by X-ray diffraction in other crystals which had less opportunity to anneal, were (3) $(110)_I || (001)_{II}$, $[10\bar{1}]_I || [010]_{II}$, in which $\angle [111]_I [001]_{II} = 27^\circ$ and (4) $(11\bar{1})_I || (100)_{II}$, $[01\bar{1}]_I || [010]_{II}$, in which $\angle [111]_I [001]_{II} = 21^\circ$, but the sense of tilt is opposite to that in relation (3). There were also grains in which $[001]_{II}$ persisted as $[111]_I$, as in relations *A* and *B*, but reflexions were too sparse and distorted for detailed analysis.

Many transformed crystals, further heated to 180°C , recrystallized with movement of a Z-shaped interface. A few recrystallized grains had regained the original optical extinction direction of form II. As these crystals were viewed down $[010]_{II}$, this observation implies either that $[111]_I$ was then tilted only around $[100]_{II}$, or $[111]_I || [001]_{II}$ as a result only of recrystallization and not as a direct result of the transformation mechanism, which in these particular specimens had produced a different orientation. The recrystallized grains gave the X-ray Laue pattern of a normal crystal. Recrystallization also removed a memory effect through which in a thermal cycle $II \rightarrow I \rightarrow II$ specimens tended to return, though aragonite-twinned, to their original orientation in II (Kennedy, Ubbelohde & Woodward, 1953).

Discussion

The lamellar texture associated with the diffuse extinction suffices to explain the opalescence observed after transformation to phase I during spectroscopic measurements (Chisler, 1966). Reported gradual weakening of the opalescence can be attributed to annealing, and the recrystallization accounts for its reported disappearance at 180°C .

The fact that specimens recrystallized shows that they stored enough energy, such as strain and twin-boundary energy, to cause recrystallization without any contribution from mechanical deformation. To supply this energy the transformation must proceed under non-equilibrium conditions. Some at least of the superheating therefore is essential for propagation. The maximum free energy which could be stored is $\Delta G = \Delta S \Delta T \approx 190 \text{ J mol}^{-1}$, where ΔT = the observed 15°C , $\Delta S_{II \rightarrow I} = 12.5 \text{ J mol}^{-1}$ (Arell, 1962).

Both the surface tilts and the rapidity of the trans-

formation which produced the lamellar texture suggest shear-like components in the mechanisms. There is now structural evidence that the change from the calcite-type to the aragonite-type of coordination of the oxygen atoms of the anion by cations may be compatible with shears and lattice deformations. Firstly, in the structure of KNO_3 I the anions are already distributed equally between calcite-type and aragonite-type orientations (Strømme, 1969). Secondly, within the same rhombohedral array of cations, the anions are almost entirely in aragonite-type coordination in KNO_3 III (Strømme, 1969). Phase III is a noncentrosymmetric distortion of I, metastable at atmospheric pressure. Kennedy (1972) examined the transformation $III \rightleftharpoons I$ in single crystals of rhombohedral morphology, by polarized-light microscopy. The transformation was apparent from the displacement of the compensation band when the quartz wedge was in place. The crystals transformed suddenly and could be cycled repeatedly with small hysteresis, no disruption and no random interface. The change from aragonite-type to calcite-type coordination of (or by) oxygen therefore may occur as an order-disorder process at or above the temperature of the lattice deformation: it does not demand a reconstructive mode of growth. In the transformation $II \rightarrow I$ the deformation of the cation array must itself cause some consequential reorientation of the anion. This will be discussed, especially for relation *B*, in a later paper. Orientations other than *A* and *B* require tilt of the anion. That a structure having dynamically disordered anions can convert by a lattice deformation with tilt of the anions is shown by the transformation RbNO_3 I \rightarrow II, which is from cubic to KNO_3 I type. This transformation is martensitic and produces fine lamellae, themselves internally twinned (Kennedy, 1970; Kennedy & Kriven, 1976). If, as has been argued here, the oxygen atoms can be unlocked from their cation coordination either by thermal motion or by displacements consequent upon the structural deformation, then the array of ion centres can be transformed homogeneously. The arrangement of ions in KNO_3 II (and in aragonite) is of almost inverse NiAs type, distorted by displacements of adjacent columns of anions by $\pm c/6$. The anions are in approximately simple hexagonal stacking. This is important: such columns will tend to fall into say *ABC* stacking, which is found in phase I. Alternatively, the structure of KNO_3 I is related to NaCl, and through its primitive cell to CsCl. Kennedy (1974) has illustrated ways in which NiAs-type can be converted to NaCl-type, either directly or through CsCl-type, without persistence of the basal plane, by lattice deformations accompanied by non-diffusive but quite large consequential displacements of one set of ions. The structure types were said to be deformationally related. Several different deformational relations are likely to be needed to explain all the orientations in KNO_3 and CaCO_3 . The lamellar texture of I observed in the present work is consistent with the operation of lattice deformations,

since these tend to produce lamellar twinning, if symmetry options are available, in order to accommodate the lattice misregistry at the interface. The same geometrical requirements in general lead to irrational orientations.

If the orientations are crystallographically controlled they should be reproducible. There has been no discussion of this. As already implied Kennedy & Kriven's (1972) results confirmed Das Gupta's (1964) *B* orientation, which had been queried by DO, but not relation *A*. In the present results, orientation (3) is the same as the DO relation: this is the first confirmation that it is reproducible. Our orientation (4) is new. Relation (1) is equivalent to BFT I, and (2) differs from BFT III by a rotation of 8° around $[010]_{II}$. This is fair agreement since combination of the experimental error quoted by BFT and by the present authors amounts to $\pm 6^\circ$.

There are some potentially significant geometrical relations between these orientations. Relations (4), (3) (=DO), and *B* have $\langle 10\bar{1} \rangle_I \parallel \langle 010 \rangle_{II}$; BFT I, III, and *A* have $\langle 10\bar{1} \rangle_I \parallel \langle 100 \rangle_{II}$. BFT I and III in CaCO_3 differ by $+6^\circ$ and -6° respectively from the orientation of a mechanical twin of relation *A*. This suggests that these might be two of the variants of a cooperative mechanism.

The observation of the BFT orientations in dry crystals implies that in natural calcium carbonate they could in principle have been due to direct thermal transformation.

The DO relation (3) has the significant feature, not hitherto discussed, that the $\{110\}_I$ plane parallel to $(001)_{II}$ is the well known mechanical twin plane. Because of the twofold symmetry of the aragonite structure (II), two symmetry options are possible and would be related by reflexion in $(100)_{II}$. Alternation of these options would constitute transformation twinning. This then is one way in which the product having threefold symmetry, forming from a parent having twofold symmetry, could be transformation-twinned.

As this transformation twinning associated with the DO orientation follows the same law as mechanical twinning of calcite, the two sources could in some cases be difficult to distinguish. One would, however, expect a martensitic subtexture based on the twinning to be more complex, as in rubidium nitrate (Kennedy & Kriven, 1976). In so far as these results are relevant also to calcium carbonate, they imply that structural trans-

formation should be regarded as a potential additional source of twinning in naturally occurring calcite coexisting with aragonite.

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