for 104 out of the 146 $hk0$ reflexions observable with Cu $K\alpha$ radiation was 0·100 when the guest molecule was assumed to be zigzag planar [observed and calculated values of $\sqrt{(\Sigma F^2)}$ were compared for the overlapping reflexions]. The n-$C_{16}H_{34}$ molecule is actually shortened by 0·66 Å within the channel [from 22·64 Å for the extended conformation (Laves, Nicolaides & Peng, 1965) to 21·98 Å]. The deformed channel, however, is able to accommodate the slightly contracted molecular chain. Although more detailed analysis of these adducts is in progress, it is deducible from the present result that the order–disorder transitions are fairly strongly co-operative.

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Structural relationships between the polymorphs of silver nitrate.

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The unique structure of $AgNO_3$ II is shown to be a substantial distortion of the $TlNO_3$ III structure. It also has topological links with the aragonite structure of KNO_3 II. When there is sufficient thermal libration of the NO_3^- ion, the structure of II can be converted homogeneously to the high-$NaNO_3$ structure of phase I. The relationship between the structures of I and II helps to explain features of the previously published kinetics of propagation in the thermal transformation $AgNO_3$ I $\rightleftharpoons$ II. Filamentary crystals of phase II have been grown. Their transformation was followed by X-ray diffraction and microscopy. The observations are consistent with operation of structural relationships. Crystals tend to return to their original orientation after a thermal cycle II $\rightarrow$ I $\rightarrow$ II.

The structure of the room-temperature phase II of $AgNO_3$, being unique, has not appeared to fit into the series of $M(XO_3)$ structures. Accordingly, and since no orientation relations were recognizable, the structural transformation $AgNO_3$ II $\xrightarrow{159°C}$ I has been accepted as reconstructive (Asadov, 1968; Asadov, Nasirov & Jabrailova, 1972). This transformation has provided exceptionally extensive data on the kinetics of advance of a phase interface in single-crystal platelets (Kennedy & Schultz, 1963). Although the rates were highly temperature-dependent, as expected for a reconstructive mechanism (reaching a maximum at 110°C and being effectively zero at −30°C), the data led Kennedy & Schultz (1963) to the view that instead of transfer of individually thermally activated ions, micro-regions of many unit cells transformed cooperatively. Such a mechanism would be possible if there existed a direct path for the structural rearrangement. The path is relevant also to recent theories which consider the possibility of a diffuse interface (*e.g.* Temkin, 1973). Elucidation both of crystal packing and of mechanisms therefore requires examination of structural relationships. In the experimental study of transformations filamentary crystals (whiskers) offer the advantages of a

relatively low number of dislocations and relatively little accumulation of transformation stresses, which can cause plastic deformation. In the present work whiskers of $AgNO_3$ have been grown and their transformation observed; and by consideration of the structures the general arrangement of ions in phase II has been shown to be topologically related to the arrangement in phase I and other nitrate structures.

$AgNO_3$ I has the high-$NaNO_3$ structure, space group $R\bar{3}m$, $Z = 1$, $\alpha = 78·0°$ (Fischmeister, 1956). This is calcite-like but has orientational disorder of the anions around their threefold axis (Strømme, 1969). The structure of phase II, symmetry $Pbca$, $Z = 8$, is predominantly ionic but distorted by the tendency of Ag to bond to O (Lindley & Woodward, 1966).

Experimental

Laue, oscillation and precession X-ray patterns were recorded before and after a thermal cycle II $\rightarrow$ I $\rightarrow$ II. The crystals were cemented to a glass fibre on the goniometer head and surrounded by a cylindrical heater. The transformation of whiskers was observed at a magnification of 250 on a polarizing microscope carrying a cine camera and fitted with a transparent glass heating stage. For both X-ray and optical work the temperature was automatically controlled to within 0·1°C. Specimens were heated at 7°C min^{-1} to 157°C, and thereafter very gradually until trans-

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formation occurred. Before cycling to II they were annealed for 20 min at 170 °C.

The crystals used were whiskers less than 0·04 mm thick. It was found that whiskers could be grown from material first recrystallized rather rapidly on filter paper from aqueous solution over $CaCl_2$ in a desiccator at room temperature. They were dried over fresh $CaCl_2$. Each crystal was used for only one thermal cycle.

Results

Untransformed phase II gave obvious thermal diffuse X-ray reflexions, which increased in intensity with temperature.

The optical observations of II → I showed a maximum superheating of 19 °C. In most crystals a single interface advanced from one end. The rate was not uniform. In slow growth the interface was seen to be jagged. The maximum rate in transformation II → I was 0·6 mm s⁻¹. A single extinction direction commonly resulted from a single interface, but in some of these crystals the extinction direction was very diffuse, suggesting finely mixed orientations. In other crystals different orientations resulted from independent nuclei.

In the transformation I → II the maximum supercooling was 43 °C, in contrast to previous measurements on platelets, some of which could apparently be supercooled indefinitely (Kennedy & Schultz, 1963). The maximum rate of propagation attained in the present work was 0·78 mm s⁻¹ at a supercooling of 28 °C. In the transformation II → I many whiskers kinked, making angles of approximately 15° especially when the rate was relatively rapid.

Combined X-ray and optical results showed that many crystals returned to their original orientation in phase II. These included specimens which had several orientations in phase I. Others, including some which had a single orientation in phase I produced several orientations in phase II.

Discussion

The kinking suggests that a shape change, indicating a shear component in the mechanism, may accompany the transformation, as in the transformation of whiskers of Fe (Zerwekh & Wayman, 1965) and of NH_4Br (Kennedy, Patterson, Chaplin & Mackay, 1974). The jagged interfaces were reminiscent of acicular or lath-like growth in martensitic transformations (which are based on a lattice deformation), and the diffuse extinction in phase I suggests the fine lamellar twinning or the mixture of variants which can result from martensitic mechanisms. The return to the original orientation could be due either to retained nuclei in a reconstructive mechanism, or to crystallographic control. There is no other evidence for the former in $AgNO_3$. In the latter case, the changes of orientations would imply symmetry options. The rates are comparable to, though somewhat slower than, those observed previously in platelets and therefore again imply some kind of coordinated displacements. This work provides somewhat more evidence for crystallographically determined than for reconstructive mechanisms and therefore suggests that relationships between the structures should be examined.

Structural relationships

The new view of the structure presented in Fig. 1(a) shows that each anion lies within an irregular coordination cage of eight cations. In this respect the structure is related to $TlNO_3$ III, which is also orthorhombic with $Z = 8$ (though of symmetry $Pnma$) and in which the CsCl-related subcells are pseudo-tetragonal (Fraser, Kennedy & Snow, 1975); and to $RbNO_3$ III in which these subcells are cubic in shape (Salhotra, Subbarao & Venkateswarlu, 1968). The difference from these structures is mainly in the orientation of the anion within the coordination cage, and in the angle of the (010) net, which is 70° in $AgNO_3$ II.

The $AgNO_3$ II structure is deformationally related also to the aragonite structure of KNO_3 II [Fig. 1(b)]. If the 70° mean angle of the (010) net of the cation array is reduced to 60°, then only minor further displacements are needed to convert the array into a sequence of regular trigonal prisms on (010) as base. The anion array also would then be simple hexagonal. Translation of the cation layer at $b/2$ through less than an ionic diameter could convert the cation array to ABA stacking while leaving the anion array approximately simple hexagonal. With accompanying adjustments to the orientations of the anions, these deformations produce the KNO_3 II structure, symmetry $Pbnm$.

Thus crystallochemically the arrangement of ion centres in the $AgNO_3$ II structure can be regarded as a substantial distortion of that in either the KNO_3 II structure or the $TlNO_3$ III structure.
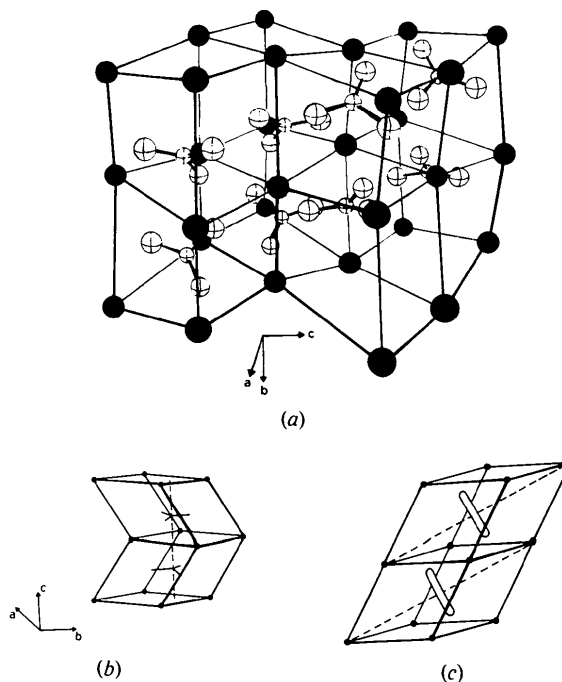

(a)

(b)   (c)

Fig. 1. (a) The structure of $AgNO_3$ II drawn to show the primitive subcells. Atoms are drawn with 50% probability ellipsoids. The data are from Lindley & Woodward (1966). The view is approximately along a. (b) Two coordination cages of the structure of KNO_3 II. (c) Two cells of the structure of $AgNO_3$ I, in which there is some disorder of the orientations of the NO_3^- ions.

Although the structures of $M(XO_3)$ crystals are due in part to the mutual coordination of O atoms and cations (Fraser, Kennedy & Snow, 1975), this coordination can be unlocked in other transformations by a reconstructive activated step without disruption of the whole framework, which can deform homogeneously to produce the new lattice. This has been shown experimentally by the mode of conversion of $TINO_3$ III to the $RbNO_3$ III structure (Kennedy & Patterson, 1965); and especially of cubic $RbNO_3$ III to the $NaNO_3$-like $RbNO_3$ II, in which the planes of the anions are quite differently oriented (Kennedy & Kriven, 1976). KNO_3 II also transforms to the high-$NaNO_3$ structure in non-random though complex ways (Kennedy & Kriven, 1972; Kennedy & Odlyha, 1977).

Transformation of $AgNO_3$ II to the high-$NaNO_3$-like structure of $AgNO_3$ I also requires sufficient oscillation of the anions to unlock the O atoms from their cation coordination. The observed thermal diffuse reflexions suggest that substantial thermal motion is available. Since the libration of a triangular anion is not pure oscillation but precession (Siegel, 1949), the required permanent tilt of the anion might be achieved without much additional activation. If the structure is regarded as related to $TINO_3$ III the remaining part of the structure change is then the homogeneous deformation of the unit cell of $AgNO_3$ II to produce eight primitive cells of I. The deformation can be regarded either as mainly the conversion of each subcell (made regular by minor displacements) to a rhombohedron by relative extension along its body diagonal, or as a shear on (010) along [001], with moderate adjustments of dimensions [Fig. 1(c)].

It follows from these relationships that lattice deformations associated with coordinated displacements of many ions should be possible in $AgNO_3$. Such structural deformations, induced in part by interaction of lattice vibrational modes with the local dislocations, are similar to those in martensitic transformations, and would suffice to explain the rapid transformation of micro-regions suggested in the previous study of kinetics. The necessity for thermal activation for reorientation of the NO_3^- ion within its cage would tend to limit the rates to finite values as observed. Such deformational structural relationships link many structure-types (Kennedy, 1974a). As previously suggested, however, martensitic accommodation at the interface might not necessarily be achieved. Not only could the inherent relationships then be obscured, but local stress-relieving relaxation processes could contribute to the measured activation energy

(Kennedy, 1974b). In this case then the activation energy could contain both this factor and the energy for reorientation of the anion. Just as coordinated displacements are feasible in this transformation, so some of the rapid advance of the phase interface, with sudden transformation of microscopic blocks, observed in early studies of kinetics (Hartshorne & Swift, 1955) may also be due to unforeseen structural correspondences.

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