The Transformation of CsCl Type ⇆ NaCl Type. Part II: Orientation Relations in Phase Transformations CsCl Type → NaCl Type in Ammonium Halides

S. W. KENNEDY

Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide 5001, South Australia, Australia

J. H. PATTERSON

C.S.R. Research Laboratories, P.O. Box 39, Roseville 2069, N.S.W., Australia

R. P. CHAPLIN*

Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide 5001, South Australia, Australia

AND

A. L. MACKAY

Department of Crystallography, Birkbeck College, University of London, Malet Street, London WC1E 7HX, United Kingdom

The polymorphic transformation CsCl type → NaCl type in ammonium chloride, bromide, and iodide is shown to be topotaxial and orientation relations derived by X-ray diffraction are reported for NH_4Cl and NH_4Br. These orientation relations are similar to those maintained in the reverse transformation NaCl type → CsCl type. At least the commonest relation can result from cooperative displacements. Transformed crystals of NH_4I and NH_4Br store stresses and imperfections sufficient to modify significantly the ideal thermodynamics of transformation.

Introduction

The primitive cubic CsCl and f.c.c. NaCl structures are related basic types but it is not clear whether or how the formal crystal chemical relationships would be manifested as topotaxy in a real transformation involving such a large change of structure and volume. As there are no previous data on orientation relations for CsCl → NaCl type transformations, studies of the crystallography of the transformation CsCl type to NaCl type complement the results on the NaCl → CsCl

type transformation presented in part I of this study by Fraser and Kennedy (1) who found orientation relations and shape changes indicating extensively coordinated displacements in NH_4Br, and those of Chatterji, Mackay, and Jeffery (2) who showed that there were several preferred orientations in specimens of CsCl transformed in the electron microscope. The mechanism of structure change on heating is not necessarily the same in detail as that of the reverse change on cooling, because greater activation energy is available in superheating than in supercooling, and because different lattice-invariant modes of accommodation might operate. Menary,

* Now at The University of New South Wales, Kensington 2033, N.S.W., Australia.

Ubbelohde, and Woodward showed that the transformation was discontinuous in cesium chloride (*3*). The present work deals mainly with the transformation from CsCl type to NaCl type in ammonium halides. It shows that orientation relations are maintained which are similar to those observed in the change NaCl → CsCl type, and that transformation stresses can break the material.

Ammonium chloride, bromide, and iodide have NaCl type packing in their highest temperature polymorph (I), and CsCl packing in form II. The equilibrium temperatures are 184, 137, and −17°C, respectively. In all three, as in CsCl, there is a large volume change $\Delta V / V_{II} = 17\%$.

Experimental

The transformations were investigated by X-ray diffraction photography and light microscopy. Laue, oscillation, and some rotation photographs were recorded, and some crystals were set in special orientations to produce expected reflections from the product. As a consequence of usual exposure times, the diffraction patterns corresponded to crystals which had been annealed for an hour or more after transformation, except that some diffraction patterns from NH$_4$I were observed directly with an intensifier (*4*). A small cylindrical wire-wound heater was mounted on the goniometer head. Individual crystals of NH$_4$Br and NH$_4$Cl were mounted in thin glass capillaries which were sealed to reduce sublimation and a glass rod inserted into the capillary supported the crystal. The microscope had a transparent heater previously described (*5*). For microscopy of NH$_4$I, magnifications up to 400 in transmitted light were obtainable with a long-working-distance objective. NH$_4$I crystals were enclosed in a small chamber which was cooled by a flow of dry cold air. Care was taken to avoid moisture within the device. The temperature was regulated manually and read with a thermocouple. Some specimens of NH$_4$I were also examined in a Philips EM200 electron microscope with cooling stage. Whilst they gave good electron diffraction patterns, nucleation was found to be very slow.

Needles of NH$_4$Cl and NH$_4$Br elongated along [001] were selected from dendrites obtained by slow cooling of aqueous solutions. They were approximately 0.2 mm thick and 1 mm long. Square platelets of NH$_4$I were grown by slow evaporation of a solution in ethanol. They were up to 1 mm wide and 0.05 mm thick. Filamentary crystals of NH$_4$Br and NH$_4$I were formed in a desiccator from crystals which had been grown relatively quickly.

Results

When NH$_4$Cl and NH$_4$Br were transformed to phase I on the X-ray apparatus, groups of individual crystallites were formed. Individual Laue reflections were sharp, indicating little plastic deformation, but the orientations were spread within ±2°, or in some specimens ±5°, of the preferred orientations stated here. Usually the spread of orientation was greater in NH$_4$Cl than in NH$_4$Br. The relation $\langle 011 \rangle_I //$ [001]$_{II}$ was always maintained, where [001]$_{II}$ was the needle axis. This was observed independently in different laboratories. The most common orientation relation was

$$(11\bar{1})_I // (100)_{II} \quad \text{A}$$
$$[011]_I // [001]_{II}.$$

Other orientations observed were

$$\{11\bar{1}\}_I // (\bar{1}\bar{1}0)_{II} \quad \text{B}$$
$$\langle 011 \rangle_I // [001]_{II}.$$

and

$$\{100\}_I // (100)_{II} \quad \text{C}$$
$$\langle 011 \rangle_I // [001]_{II}.$$

When specimens were cooled back to the room-temperature form, many regained the original orientation: the needle axis always became [001]$_{II}$ again. On the microscope the dendritic crystals of NH$_4$Br expanded markedly along the needle axis, [001]$_{II}$, and were sometimes deformed during the transformation to phase I. Many filamentary crystals of NH$_4$Br bent successively or curled. Some became S-shaped and developed steps on the surface having traces transverse to the crystal, parallel to [010]$_{II}$. Several kinked sharply

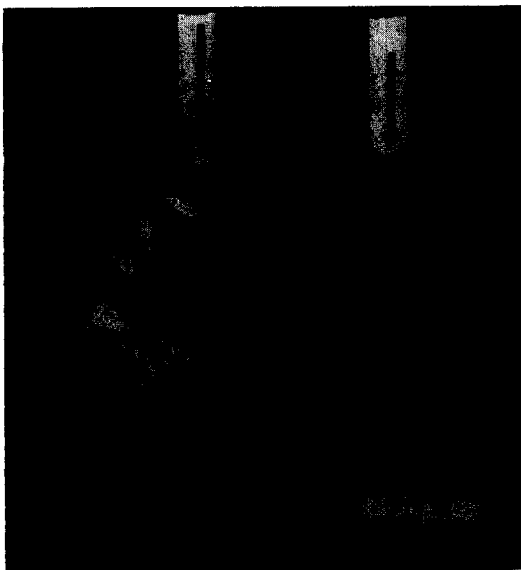FIG. 1. Shape of a previously straight crystal of NH_4Br II 0.05 mm thick, after transformation to phase I.

FIG. 2. An interface (arrowed) advancing from the top corner during the transformation II→I. Interference contrast illumination.

at an interface, the regions between kinks remaining straight, as shown in Fig. 1. The angle of bending at the kink was 35°. When some rectangular platelets of NH_4Br (originally grown in phase I but transformed to and annealed in phase II) were transformed from phase II to I at only slight superheating, a curved interface advanced continuously and approximately radially from one corner. The rate was temperature dependent. The crystals expanded parallel to the $\langle 110 \rangle_I$ bisecting the corner, which consequently became acute (Fig. 2). The changing of shape after the passage of the interface occupied a just-detectable finite time. Crystals cracked slowly within 2 min after passage of the interface. When several crystallites had resulted from the transformation, the cracking occurred preferentially but not only at the grain boundaries.

The reverse transformation, or the cycle I→II→I, was examined in ammonium iodide. On the microscope the platelets transformed with little delay at −25°C. The interface was curved. Occasionally a very faint interface region was thought to precede the main one. The crystal retained its general shape. After 15 min at −25°C however, cracks began to develop, and ultimately the crystal shattered into several fragments. When crystals were transformed completely on the microscope, then cycled back to phase I before cracking began, the subsequent X-ray pattern showed that they returned to the original orientation (which was known from optical observation of the $\langle 100 \rangle$ edges), but this orientation was randomized over a detectable range of 7°. When the cycle was performed on the image intensifier goniometer, there was little pattern immediately after transformation to phase II, but some reflections appeared after 30 min. When the crystal was returned to phase I, the pattern reappeared immediately, with some asterism, but annealing continued and reflections became sharper over a period of 40 min at 22°C. Further annealing continued at 40°C. It is evident from these continued changes that, initially, the product of transformation is not at all in an equilibrium minimum energy state.
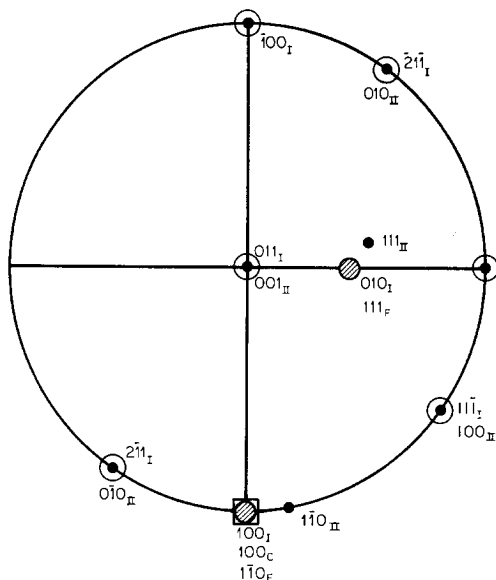
FIG. 3. Stereographic projection of the orientation relations A (denoted by ⊙) and C, for the transformation NH_4Br II → I, compared with relation A for the transformation I → II. The subscript F denotes phase II in the transformation I → II (◉).

FIG. 4. A total lattice deformation which transforms primitive cubic to f.c.c. The plane of the paper is {110} of both structures. A {110}$_{II}$ plane is shaded in the cell of II and the shaded plane in the cell of I is {11$\bar{1}$}. The lattice deformation is a pure strain having [111] as principal axis, combined with a rotation of 19.48° to keep the {110} plane in its original orientation. This is equivalent to a shear on (110)$_{II}$ combined with another differential dilatation. Two symmetry options for the ⟨111⟩ principal strain-axis are shown. The cells are drawn in approximately the correct relative scale.

Discussion

The fact that the orientation relations were reproduced in both NH_4Br and NH_4Cl indicates that they were structurally controlled. This conclusion is supported by the similarity to relations observed in the transformation I→II. The present relation A is close to the main orientation A found by Fraser and Kennedy (1) for NH_4Br I→II. The two are compared in Fig. 3. Relation C approximates to the relation C for NH_4Br I→II, and is the relation in an analogous though indirect change NaCl-like→CsCl-like in $RbNO_3$ (6), and also includes the preferred orientations {001}$_I$//{001}$_{II}$ detected in CsCl I→II by Chatterji et al. (2) and by Pöyhönen, Jaakola, and Rasänen (7) using electron diffraction. One of the equivalents of relation B differs from relation C by a rotation of 5°.

Relation A could be produced by coordinated displacements. The conventional lattice correspondence for this transformation is based on the fact that the primitive cell of the f.c.c. lattice is rhombohedral: its [111]
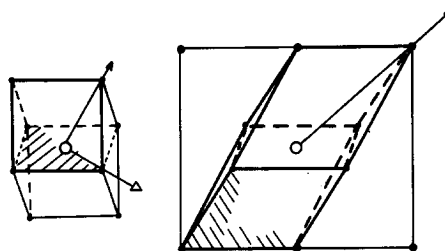
direction coincides with $[111]_{f.c.c.}$, its ⟨100⟩ axes are ⟨110⟩$_{f.c.c.}$, and its faces are the {11$\bar{1}$}$_{f.c.c.}$ planes; the {110}$_p$ not containing a ⟨111⟩ are {100}$_{f.c.c.}$ (Fig. 4). A primitive cube, such as the CsCl cell, is converted into this rhombohedron by a differential extension along [111] with contraction normal to this direction. The {1$\bar{1}$0} plane containing the [111] strain axis is unrotated by the strain. It is to be noted, however, that planes containing the principal strains (dilatation and contraction) will be planes of maximum misfit and therefore unlikely to remain common to the two structures. If the lattice deformation of the primitive cube occurs while keeping the (110)$_{II}$ plane unrotated, then $[011]_I$// $[001]_{II}$ (Fig. 4). This total lattice deformation is the pure strain combined with a rotation of 19.48° around [$\bar{1}$10]$_{II}$. It involves a component of shear on (110)$_{II}$, but the shear is only one component of the lattice deformation. The resulting orientation relation is $[011]_I$// $[001]_{II}$, (100)$_I$//(110)$_{II}$. (This relation was observed by Chatterji, Mackay, and Jeffery (2) in CsCl I→II.) If, however, in adjacent regions there operate alternative ⟨111⟩ strain axes related by reflection in (100)$_{II}$, then this (100)$_{II}$ net (which becomes a (11$\bar{1}$)$_I$ net) is common to both twin components. Formally, this introduces a further rotation of the two
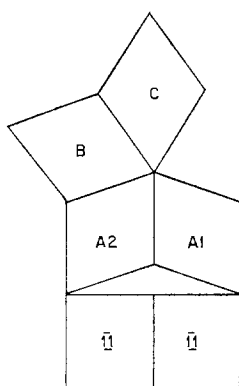
FIG. 5. The observed relative orientations of phase II and phase I in NH_4Br, and the way in which the orientations might be produced by changes of twinning option. The cubes marked II represent primitive cubic cells of phase II, the rhombohedra are the corresponding primitive cells in the product phase I. The rhombohedra A_1A_2 are in orientation A of the text, B is one possible variant of orientation B (the other is close to C), and C is in orientation C. All have $[011]_I//[001]_{II}$ normal to the paper. If regions B or C were produced previously, the formation of A_1A_2, using a different equivalent $\{11\bar{1}\}_I$ twin plane, would rotate them into the orientation shown.

strain axes around the original $[011]_{II}$ direction to allow the twins to share this $(11\bar{1})_I$ net (Fig. 5). The resulting orientation relation is $[011]_I//[001]_{II}$, $(11\bar{1})_I//(100)_{II}$. This is the commonly observed relation A. In practice, such twinning might occur if it provided a lattice-invariant shear needed to accommodate the mismatch between the two structures (8). If it occurred on a very fine scale, however, it would produce a high-energy faulted structure. This mechanism may nevertheless be favored because it keeps a close-packed direction, $[011]_I$, common to the two structures, and the spacing between the sets of parallel planes $(100)_{II}$ and $(11\bar{1})_I$ contracts only slightly from 4.08 to 3.96 Å. As the lattice transformation produces a change in the angle between the faces of the primitive cell from 90 to 70.5°, successive changes of twinning option at the interface would tilt already transformed regions through angles $= 2(90 - 70.5) = 39°$ which would produce orientations of general type B, and when repeated, type C. The kink angle in the whisker shown in Fig. 1 is only

4° less than the angle expected from such twinning neglecting any shape modification due to lattice-invariant shears in the straight regions. In general, random successive changes of option may explain the bending and curling of whiskers.

However, relations B or C (which, if differing by 5°, are not distinguished within the precision that has been available) occur more commonly as noted above, especially in $RbNO_3$ which produces oriented platelets. This relation suggests a rearrangement of the stacking sequence parallel to $(100)_{II}$, the net remaining square but spacings in it increasing from $a_{II} = 4.09$ Å to $[011]_I = 4.85$ Å. Decision between alternative geometries must await further data including some on the type of shape deformation, but Fraser and Kennedy (1), whose main relation was of the A type, did show that regular shape changes were produced in the lower-temperature region. Activated rearrangements (which may be indicated by the observed temperature dependence of growth) may help to provide accommodation at temperatures near and above the equilibrium temperature. This would be consistent also with the kinetics observed in the higher part of the temperature range in the corresponding pressure-induced transformation in KCl (9).

The observations on NH_4I show that larger stresses were stored in form II just after transformation, and indicate a high degree of imperfection. The delayed cracking is consistent with the presence of variants which were mutually constrained because of opposing shape changes until cracks ultimately nucleated and grew. The constraints (10) and energy stored in defects (11) must modify significantly the net free-energy change and the local equilibria for such transformations. Since recovery proceeded at higher temperatures in NH_4I, the sharpness of the X-ray reflections from NH_4Cl and NH_4Br would also indicate such annealing.

Whilst there are also in ionic crystals such as $AgNO_3$ transformations which show very pronounced thermal activation of the rearrangement with little sign of topotaxy (11), the present measurements on ammonium halides again show that a large change of

structure accompanied by a large volume change can be achieved topotaxially.

Note added in proof. In part III (*12*) computations according to martensite theory predict orientations of type A for the reverse transformation I to II, but again require rotations of reverse transformation I to II, but again require rotations of macroscopic regions, as suggested here, to produce relation C.

Acknowledgments

References

1. W. L. FRASER AND S. W. KENNEDY, *Acta Cryst.* **B28**, 3101 (1972).

2. S. CHATTERJI, A. L. MACKAY, AND J. W. JEFFERY, *J. Appl. Cryst.* **4**, 175 (1971).

3. J. W. MENARY, A. R. UBBELOHDE, AND I. WOODWARD, *Proc. Roy. Soc.* **A208**, 158 (1951).

4. S. W. KENNEDY, *Nature* **210**, 936 (1966).

5. S. W. KENNEDY AND J. H. PATTERSON, *Proc. Roy. Soc.* **A283**, 498 (1965).

6. A. J. IVERSEN AND S. W. KENNEDY, *Acta Cryst.* **B29**, 1554 (1973).

7. J. PÖYHÖNEN, S. JAAKOLA, AND V. RASÄNEN, *Annal. Univ. Turku. Ser.* **A80** (1964).

8. A. KELLY AND G. W. GROVES, "Crystallography and Crystal Defects," Longmans, London (1970).

9. L. D. LIVSHITZ, YU. N. RYABININ, L. V. LARIONOV, AND A. S. ZVEREV, *Zh. Eksp. Teor. Fiz.* **55**, 1173 (1968); *Soviet Physics JETP* **28**, 612 (1969).

10. A. R. UBBELOHDE, *Nature* **169**, 832 (1952).

11. S. W. KENNEDY AND P. K. SCHULTZ, *Trans. Faraday Soc.* **59**, 156 (1963).

12. W. L. FRASER AND S. W. KENNEDY, *Acta. Cryst.* **A30**, 13 (1974).