

Acta Cryst. (1972). B28, 3101

The transformation $Fm\bar{3}m$ to $Pm\bar{3}m$ in ammonium bromide. By W. L. FRASER and S. W. KENNEDY, *Physical and Inorganic Chemistry Department, University of Adelaide, Adelaide 5001, Australia*

(Received 15 May 1972)

Orientation relations are reported for the transformation NaCl type to CsCl type in single crystals of NH_4Br . The transformation produces shape changes. The observations indicate a displacive mechanism which rotates the $[111]$ direction which could be common to these lattices.

The crystallographic studies of the structural transformation NaCl type \rightleftharpoons CsCl type so far reported show that the change is discontinuous but have not otherwise provided definite evidence about the type of mechanism involved. Caesium chloride was examined in most of these. Here we report X-ray and optical observations of the corresponding transformation I ($Fm\bar{3}m$) to II ($Pm\bar{3}m$) in ammonium bromide. Some topotactic relation is expected because the primitive cubic and face-centred cubic lattices are simply related through the primitive rhombohedron of the f.c.c. lattice. Buerger (1951, 1961) suggested that only a contraction down the common $[111]$ direction was needed, and that this would require no energy barrier. Chatterji, Mackay & Jeffery (1971) reported partial orientation relations for CsCl I \rightarrow II and concluded that these did not correspond to the Buerger relation.

Single crystals of NH_4Br I were grown from ethylene glycol solution above 137°C (the equilibrium temperature) on glass cover-slips. They were accurately rectangular (or square) platelets about $0.05 \times 0.05 \times 0.005$ mm in size, showing cube faces. Form I was usually oriented on the X-ray camera while at 150°C . Front-reflexion Laue and oscillation X-ray patterns from undisturbed crystals on the glass provided orientation data, and light microscopy at 400 magnification showed shape and surface effects.

Most crystals supercooled to room temperature. Some persisted in phase I at room temperature for two days. When phase II ultimately appeared it grew very rapidly in all supercooled specimens. A regular shape change was then evident in some. Either the platelet became rhombus-shaped with a new inter-edge angle for example 80 and 82° in different specimens, or two blocks within a specimen were tilted to form a dihedral angle with approximately a $\langle 110 \rangle$ direction on the original cube face in common. Many of the crystals were strained and some ultimately developed cracks which resulted in a change of relative orientation of neighbouring regions amounting to several degrees.

It proved possible to interpret two of the several orientations usually present in any one specimen. The orientation relations, stated in the nearest rational indices, are within several degrees of

$$(001)_I \parallel (1\bar{1}1)_{II}, [010]_I \parallel [\bar{1}01]_{II} \quad (A)$$

$$(100)_I \parallel (23\bar{3})_{II}, [010]_I \parallel [\bar{6}51]_{II} \quad (B)$$

$$(001)_I \parallel (023)_{II}, [010]_I \parallel [100]_{II} \quad (C)$$

In all these a $\langle 111 \rangle$ direction has rotated 14 – 25° . A was reproducible: there was one confirmed example of B and

one of C . These relations show topotaxy. The rapid propagation at large supercooling and the regular shape changes suggest that it was achieved cooperatively. There are indications of a similar mechanism in the reverse change II to I. Preliminary results by Chaplin & Kennedy (unpublished) showed that filamentary crystals (whiskers) of II kinked sharply, as would be expected at a junction of options, and the product I was oriented with $[110]_I \parallel [100]_{II}$.

Consideration of the actual lattice parameters, reported by Pöyhönen, Mansikka & Heiskanen (1964) shows that a simple contraction along $[111]$ does not interconvert the structures: a 19% uniform expansion of I normal to $[111]$ is also needed. As the phases therefore do not fit in a continuous manner in this orientation some energy barrier is to be expected. A lattice correspondence combined with a big structural misfit provides an appropriate example to test the extent to which martensite theory (Kelly & Groves, 1970) applies. At this stage graphical martensite analysis (Fraser & Kennedy, 1972), assuming the Buerger correspondence, yields predictions which do agree reasonably with orientations A and B and with the shape changes; for example the quoted inter-edge angle changes compare with two distinct theoretical solutions, 79.5 and 82.3° .

It appears that the transformation from the NaCl type structure to the CsCl type at atmospheric pressure can be cooperative, and produces a relative orientation of the actual structures which differs significantly from the relation implied in the simple lattice correspondence alone.

Thanks are due to the Australian Research Grants Committee for support.

References

- BUERGER, M. J. (1951). In *Phase Transformations in Solids*. Edited by R. SMOLUCHOWSKI, J. E. MAYER and W. A. WEYL. New York: John Wiley.
- BUERGER, M. J. (1961). *Fortschr. Miner.* **39**, 9.
- CHATTERJI, S., MACKAY, A. L. & JEFFERY, J. W. (1971). *J. Appl. Cryst.* **4**, 175.
- FRASER, W. L. & KENNEDY, S. W. (1972). Abstract Roy. Austral. Chem. Inst., Solid State Conference, Adelaide, May 1972. To be published.
- KELLY, A. & GROVES, G. W. (1970). *Crystallography and Crystal Defects*. London: Longman.
- PÖYHÖNEN, J., MANSIKKA, K. & HEISKANEN, K. (1964). *Anal. Acad. Sci. Fenn. Ser. A. VI Physica*, No. 168.