Mechanisms of Thermal Transformation of Zinc Blende to [NaCl] in MnS Crystals

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Single crystals of zinc blende phase MnS transform at 200°C to single crystals of [NaCl] phase by single diffusive jumps of the cations. Dimensional changes cause random distortion of the crystal. Evidence is also presented for a second structural correspondence in which {111} zinc blende planes become {100} [NaCl] planes. The corresponding deformational mechanism might be favored at low temperatures.

Introduction

As zinc blende and rock salt structures are simple examples of fourfold and sixfold coordination in predominantly ionic crystals, the mode of their interconversion in a crystal structural transformation is of interest for theory of transformations in both MX compounds and other crystals containing these coordinations. The structure changes zinc blende → rock salt and wurtzite → rock salt normally occur at high pressure. They are known in several MX compounds and have been the subject of various pressure studies (1, 2). In the present work crystallographic features of the zinc blende → rock salt transformation in single crystals have been investigated at normal pressure by use of metastable phases.

MnS has three forms, rock salt (α), zinc blende (β), and wurtzite (γ). Only α is stable under normal conditions, but by suitable techniques all can be grown at room temperature and pressure. The metastable phases transform to α at 200 to 400°C (2, 3).

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MnS is substantially ionic (4). The transfer of the cations to the larger octahedral sites allows a reduction in the S–S distance from 3.99 to 3.69 Å, the volume ratio V_α/V_β being 0.81. This is a rather large volume change for transformations.

Since in both structures the ions are arrayed as in cubic close packing, the transformation could, in principle, be effected merely by hopping of each Mn^{2+} ion from its tetrahedral to an adjacent octahedral site, but this might occur either at a phase interface or randomly throughout the crystal, producing an intermediate structure. If transformation occurs at an interface, while maintaining the sulfur array, then a 7.5% misregistry in dimensions is to be accounted for. In most investigated transformations where there is a lattice correspondence ("deformational transformations") the strain which transforms the lattices includes both extension and contraction, which provide at least a line of fit and which, when symmetry is reduced, may alternate to reduce accumulation of misregistry. In MnS transforming $\beta \rightarrow \alpha$ by hopping of cations such a mode of accommodation is not available since the

contraction is uniform in all directions. Experiment should show how far disruptive stresses result or, alternatively, whether propagation depends on short-range diffusion of both ions.

Although only one diffusional step is required for each cation and the structure change can therefore propagate readily at 200°C, this is nevertheless an activated process. Yet the zinc blende → rock salt transformation proceeds quite rapidly in CdTe under pressure (5). It is not clear whether sufficient driving force would cause the single step of diffusion for all cations at or below room temperature or whether a nondiffusional mechanism would operate. Kennedy showed that formally the structures could be interconverted by structural deformation (6). While this is expected to be a low-temperature mechanism, evidence for it has been found in the heating experiments described here.

Experimental

Crystals were grown in silica gel by reaction of $(CH_3COO)_2Mn$ with Na_2S or H_2S (7). Growth time was 3 to 4 weeks. Crystals mostly up to 50 μm but some 0.2 mm wide were obtained. They were of two habits: some showed {111} and {100} faces; others which were smaller were near perfect cubes. Crystals of β-phase were distinguishable from α phase by their transparency and orange color. A smaller proportion of γ crystals was present but identifiable under the polarising microscope. The well-formed β crystals did not show any γ inclusions and were stable when kept in a desiccator. They were investigated by Laue and precession X-ray photography using Mo radiation, Zr-filtered for the precession photographs; by light microscopy including darkfield and interference contrast; and by scanning electron microscopy in an ETEC Autoscan SEM. The light microscope was fitted with a small heater made from a silica coverslip coated

with indium oxide (In_2O_3). Temperature gradients were negligible.

Crystals for X-ray diffraction were selected by polarized light microscopy and appeared free of γ phase. They were mounted with epoxy resin, heated with a simple coil heater, and monitored at 200X through a microscope attached to the precession camera. Specimens were allowed to transform only partly, over a period of 1 to 4 min. They were then returned to room temperature. Some were reheated and further transformed. Observed spacings were consistent with the published lattice parameters: for α, $a = 5.223$ Å (8); for β, $a = 5.601$ Å, and for γ, $a = 3.985$ Å, $c = 6.45$Å (3).

Results

The product α structure was found to be oriented in two ways relative to the β. In the predominant orientation (type A), corresponding planes were parallel (Fig. 1a). The orientation of α was spread over 15° in moderately transformed crystals and this spread increased when they were further transformed (Fig. 1b). A second orientation (B) was present in smaller quantity. The diffraction patterns showed {100}$_\alpha$‖{110}$_\beta$ and near to {111}$_\beta$. Precession and Laue photographs from several settings were consistently indexed to yield the orientation relation, $(001)_\alpha$‖$(011)_\beta$, $[1\bar{1}0]_\alpha$‖$[100]_\beta$. This relation also implies $(100)_\alpha \,\hat{}\, (11\bar{1})_\beta = 9°$.

Also present were faint reflections which could be indexed as due to γ phase in the conventional orientation $[0001]_\gamma$‖$[111]_\beta$, $(11\bar{2}0)_\gamma$‖$(1\bar{1}0)_\beta$. Precession photographs, however, did not show the streaking which would have indicated random stacking faults in β.

On the microscope the growing α phase was readily identified by its very dark green color in contrast to the transparent orange β phase. Crystals transformed at around 200°C, the temperature of initiation differing by about 10°C between different crystals.
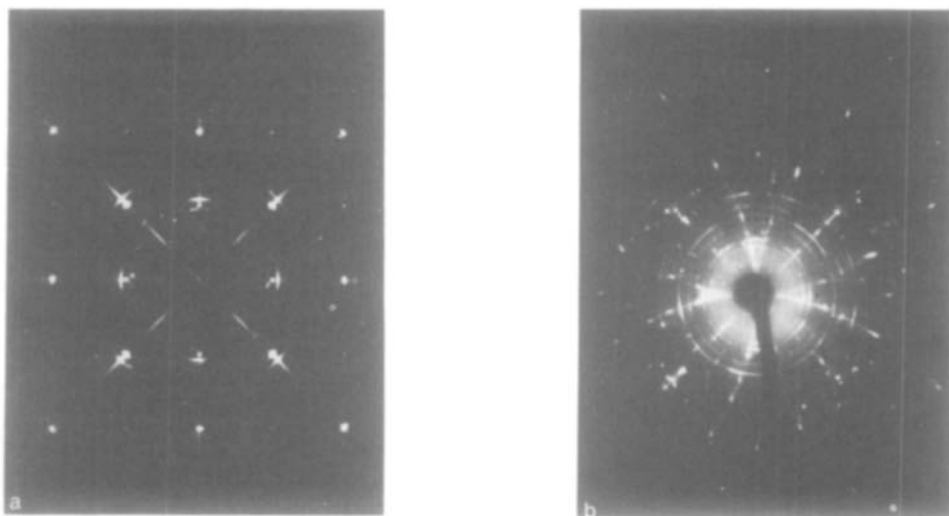
FIG. 1. (a) Precession pattern, $[001]_\beta$, showing α-MnS planes aligned with corresponding β planes, and also $(200)_\alpha$ on the $(220)_\beta$ row. Some faint reflections have been lost in reproduction. (b) Laue photograph, near to $[001]_\beta$ projection, of a crystal which was more extensively transformed, showing considerable randomization of orientation.

Two types of propagation were observed. In the first the transformation proceeded randomly from an edge with fine filaments of product advancing into the matrix. In these the surface became irregularly rumpled.

In other crystals the transformation proceeded by formation of fine parallel contiguous lamellae. In the early stages most lamellae were less than 10 μm in length, but typically some extended nearly across the crystal. After further transformation the longer lamellae, which also became wider, showed tilting of the surfaces. With slight increase of temperature a burst of transformation occurred in small regions. There were three families of lamellae mutually at an angle of 60° and in one instance lamellae at 25° to these as seen on a 111 face. These lamellae were not attributed to γ phase since they did not appear birefringent. Because of irregular edges on these crystals the traces could only be followed on one face. A small block of γ formed in one crystal which had lamellae elsewhere. Application of stress at room temperature produced laths of birefringent γ phase.

Crystals which had been transformed to α and returned to room temperature began to develop fine cracks 2 hr after transformation and must therefore have retained internal stresses.

Scanning electron micrographs of previously transformed gold-coated crystals showed, besides some irregular wave-like distortion, a series of cracks, most of which were parallel. As viewed on a 111 face they were consistent with traces of {100} planes, which are the cleavage planes of the NaCl structure-type.

Discussion

The existence of two types of orientation relation and the observations by light microscopy suggest that two different mechanisms can operate.

The predominant one, corresponding to orientation A, is the diffusive hopping of cations. This might occur within a transformation front of finite thickness, with gradual reduction of the lattice parameter, but it is unlikely that the spacings would be

reduced significantly until most of the tetra-hedral sites had been vacated. At a sharp interface, edge dislocations must be intro-duced 14 lattice repeats apart, in orthogonal directions. At the semicoherent boundary the product lattice would be tilted about 4° relative to the parent. Such tilts occurring in either sense along different equivalent directions, together with the high density of dislocations introduced by the misfit could explain much of the observed spread of X-ray reflections. Such a combination of stresses and dislocations could lead to the observed microcracking, which in turn means that a material of increased surface area has been produced.

The other orientation B implies another structural correspondence. An appropriate deformation, adapted from one proposed by Kennedy (6) is shown in Fig. 2. A set of {111} planes shears homogeneously to alter the stacking to that of {100} planes simul-taneously with dimensional changes which convert the 60° {111} nets to 90° nets and adjust the spacing. Thus, both the sets of {111}$_\beta$ shown shaded in Fig. 2 become {100}$_\alpha$. By the change in shape of their co-
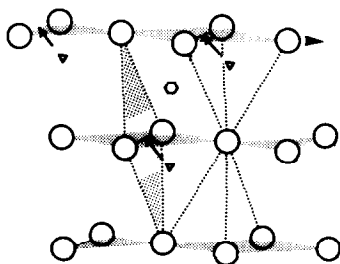

FIG. 2. Relationships for conversion of the zinc blende (β) to the [NaCl] (α) structure. The shaded planes are {111}$_\beta$. In the diffusive mechanism each cation on a tetrahedral site (triangle) jumps through the face of the tetrahedron to an octahedral site (hexagon). In the deformational mechanism the horizontal {11$\bar{1}$} planes shear as shown by the arrow head, while expand-ing relatively approximately normal to the paper. The shaded planes become {100}$_\alpha$ planes. As a consequence cations are displaced onto the middle of the former edge of the tetrahedron, a position which has become an octahedral site.

ordination cage the cations are displaced into the nascent octahedral sites. This deformation inherently requires neither dislocations nor diffusion.

It does not, however, specify what planes or directions are to remain unrotated in the real crystal. If the horizontal shaded (11$\bar{1}$) plane in Fig. 2 is kept unrotated the orien-tation relation is close to that observed, differing by a rotation of 9° in the plane of the paper. A basis for such an orientation rela-tion appears when it is noted that the (11$\bar{1}$)$_\beta$ and (010)$_\alpha$ nets are of the same area, 27 Å^2. The spacing change normal to (11$\bar{1}$)$_\beta$ does, as it should, equal the relative volume change, 19%. The (11$\bar{1}$)$_\beta$ plane, having threefold symmetry, has three options for the [011] extension and [2$\bar{1}$1] contraction axis, and thus provides the possibility of alternat-ing extensions and contractions to prevent accumulation of misregistry. Moreover, the {11$\bar{1}$}$_\beta$ net and its product (010)$_\alpha$ contain unextended vectors of the plane distortion. These are at 53.1° to ⟨011⟩$_\beta$ and 37.6° to ⟨001⟩$_\alpha$, a difference of 15.5°. Since two ⟨110⟩$_\beta$ at 60° become ⟨110⟩$_\alpha$ at 90°, each swings through 15° in the particular case where the third, [001]α, is unrotated, as observed. This is thus the angle required to make parent and product unextended vectors coincide. These factors provide means of accommodating the two structures. It does not strictly follow that (11$\bar{1}$)$_\beta$ is the interface. In the observed orientation two {010}$_\alpha$ planes each deviate equally by 9° from their parent {111}$_\beta$ planes. Thus, the angular difference between parent–product pairs is averaged, and (0$\bar{1}$1)$_\beta$ is unrotated. The observed lamellae are consistent with either {111}$_\beta$ or {011}$_\beta$ as the interface. It is clear, however, that trans-formation could proceed cooperatively by this correspondence B. At low temperatures the mechanism could, in principle, be martensitic. That 60° nets can change cooperatively to 90° nets as required here has been demonstrated in the [NaCl] → [CsCl] type transformation (9, 10).

The proposed lattice deformation B is of the type which would be favored by anisotropic stress. There was nevertheless no evidence from microscopy that B mechanism was initiated by the tensile stresses due to the A mechanism, since the two modes of transformation appeared to be able to operate independently. It follows, however, that the nonhydrostatic stresses present in some pressure cells could produce the B mechanism.

The formation of some γ phase in some specimens is consistent with Fleet's conclusion that the wurtzite structure should be somewhat more stable than the zinc blende in MnS (11).

It can be concluded that β-MnS can transform to α by two mechanisms, one controlled by cation diffusion, the other nondiffusive. The presence of the corresponding two mechanisms is more evident in the transformation of γ- to α-MnS, when the crystals are heated relatively rapidly (12). The possibility of different mechanisms for a transformation has been suggested before (13). Several mechanisms are found in the aragonite to calcite-like transformation of KNO_3 (14–16). Transformations cannot be assumed to have a unique mechanism applying under different conditions. In the present example, mechanism B provides a potential mode of relatively rapid transformation of zinc blende → rock salt at lower temperatures under pressure.

References

1. S. C. Yu, I. L. Spain, and E. F. Skelton, *Solid State Commun.* **25**, 49 (1978).
2. C. J. M. Rooymans, *Advan. High Press. Res.* **2**, 1 (1969).
3. S. Furuseth and A. Kjekshus, *Acta Chem. Scand.* **19**, 1405 (1965).
4. H. Franzen and C. Sterner, *J. Solid State Chem.* **25**, 227 (1978).
5. W. C. Yu and P. J. Gielisse, *Mater. Res. Bull.* **6**, 621 (1971).
6. S. W. Kennedy, *J. Mater. Sci.* **9**, 2053 (1974).
7. H. Schnaase, *Z. Physik. Chem.* **B20**, 89 (1933).
8. R. L. Clendenen and H. G. Drickamer, *J. Chem. Phys.* **44**, 4223 (1966).
9. W. L. Fraser and S. W. Kennedy, *Acta Crystallogr.* **B28**, 3101 (1972).
10. S. W. Kennedy, *J. Solid State Chem.*, in press.
11. M. E. Fleet, *Mater. Res. Bull.* **11**, 1179 (1976).
12. S. W. Kennedy, E. Summerville, J. D. Pockett, and P. K. Schultz, in preparation.
13. S. W. Kennedy and J. H. Patterson, *Proc. Roy. Soc. London Ser. A* **283**, 498 (1965).
14. S. W. Kennedy and M. Odlyha, *Acta Crystallogr. A* **33**, 168 (1977).
15. S. W. Kennedy, W. M. Kriven, and W. L. Fraser, in "ICOMAT 79: Proc. Int. Conf. Martensitic Transformations," (W. S. Owen, ed.), Cambridge, Mass., U.S.A. (1979).
16. W. M. Kriven, Ph.D. thesis, Adelaide (1976).