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Topotaxic phase change in Na_2SO_4.

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By single-crystal X-ray techniques, the phase transition III → I in Na_2SO_4 has been shown to be topotaxic in nature in both forward and reverse directions. The crystallographic relation between the two forms is established.

In some reactions of crystalline solids, the structures are partly preserved and thus the structure and crystallographic orientation of the starting material may control the orientation and even the nature of the products (Dent Glasser, Glasser & Taylor, 1962). One such process is topotaxy, in which a single-crystal starting material is converted into a pseudomorph containing one or more products in a definite crystallographic orientation, the conversion taking place throughout the volume of the crystal. Pseudomorphs formed from single crystals vary greatly: in one extreme the product has crystallinity comparable to that of the starting material though with deterioration, while in the other extreme the product is amorphous. Thus, opinion differs regarding the definition of topotaxy: Lotgering (1959) and Mackay (1960) have given different definitions. The phase change we describe in Na_2SO_4 fits either of these definitions equally well.

Na_2SO_4 has two crystallographic transitions according to the scheme (Kracek, 1929; Goyal, Deshpande & Karkhanavala, 1971):

$$\mathrm{V} \xrightarrow{480\,\mathrm{K}} \mathrm{III} \xrightarrow{521\,\mathrm{K}} \mathrm{I} \quad .$$

orthorhombic orthorhombic hexagonal

The crystal structures of these modifications have either been worked out from single-crystal data or inferred from powder X-ray data in conjunction with known structures of isomorphous compounds (Bredig, 1942; Fischmeister, 1954).

We grew single crystals of Na_2SO_4 from aqueous solution at different temperatures from 313 to 343 K. At all temperatures we obtained both prisms of V and needles of III. At lower temperatures, predominantly prisms of V are obtained while at higher temperatures more needles were obtained. Needles of III were found to be stable in dry air indefinitely. Fig. 1 show a micrograph of these two types of crystal.

A microscopic examination of prisms (form V) heated above the V → III transition and cooled back to room temperature showed that they lost their transparency and became clouded indicating possible formation of microcrystallites. Needles (form III) heated above the III → I transition and cooled back to room temperature remained transparent. From the inferred structures of the three modifications of Na_2SO_4, it appears that structurally the V → III transition involves a major change, while the III → I transition does not. Hence the III → I transition was studied by single-crystal high-temperature X-ray diffraction.

The Nonius Weissenberg camera had facilities for heating the crystal up to 575 K. Room-temperature oscillation and Weissenberg photographs of a needle of III were taken. These could be indexed in terms of the space group and orthorhombic unit cell proposed earlier. Without disturbing the mounting, the crystal was heated and the oscillation and Weissenberg photographs were recorded at about 550 K, *i.e.* above the III → I transition. These photographs are shown in Figs. 2 and 3. The photographs show the following. (*a*) *c* remains the same for III as well as for I, *i.e.* the twofold axis of the orthorhombic unit cell of form III transforms as the threefold axis of the hexagonal unit cell of form I. The actual magnitude of *c* increases. (*b*) The original orthorhombic unit cell has a pseudo-hexagonal symmetry with reference to the (*hk*0) reflexions (Fig. 3). During prolonged heating for about 4 h to obtain the Weissenberg photographs, the crystal fragments and the extra reflexions seen in the photograph (Fig. 3*b*) are due to misorientation of these fragments along the needle axis. On cooling to room temperature the patterns obtained are identical to those of the original orthorhombic form III, the starting material. Nonetheless, *c* of III shrinks as the temperature is increased, as is seen on the oscillation photographs at intermediate temperatures. The actual value obtained at 483 K for *c* is 6·91 (1) Å. The known cell parameters and space group of the three forms of Na_2SO_4 are given in Table 1.

Table 1. *Phase transformations in* Na_2SO_4

Phase	Cell parameters (Å) *a*	*b*	*c*	Space group
V	5·863	12·304	9·821	*Fddd*
III	5·592	8·926	6·953	*Cmcm*
I	5·385	—	7·260	?

The fact that in form III, *c* shrinks with increasing temperature and *c* for form I is larger than that for form III indicates that there should be a sudden jump in *c* at the transition temperature. The lattice relation of the phase transformation is: the repeat distance along [110], *i.e.* $\frac{1}{2}d(110) = 5{\cdot}265$ Å, and the angle between [110] and [$\bar{1}$10], 116°, of the pseudo-hexagonal Na_2SO_4 III change to 5·385 Å and 120° of the hexagonal form I, while the *c* axis of Na_2SO_4 III of 6·953 Å changes to 7·260 Å and this axis remains the same in both phases. This can be described as

$$\begin{aligned} &[110]_{\mathrm{III}} \quad 11l \quad [100]_{\mathrm{I}} \\ &[\bar{1}10]_{\mathrm{III}} \quad 11l \quad [010]_{\mathrm{I}} \\ &[001]_{\mathrm{III}} \quad 11l \quad [001]_{\mathrm{I}}\,. \end{aligned}$$

Fischmeister (1962) has discussed in detail the structural relation between forms III and I.

The present note shows that in Na_2SO_4 the III → I transition is topotaxic in both forward and reverse directions.

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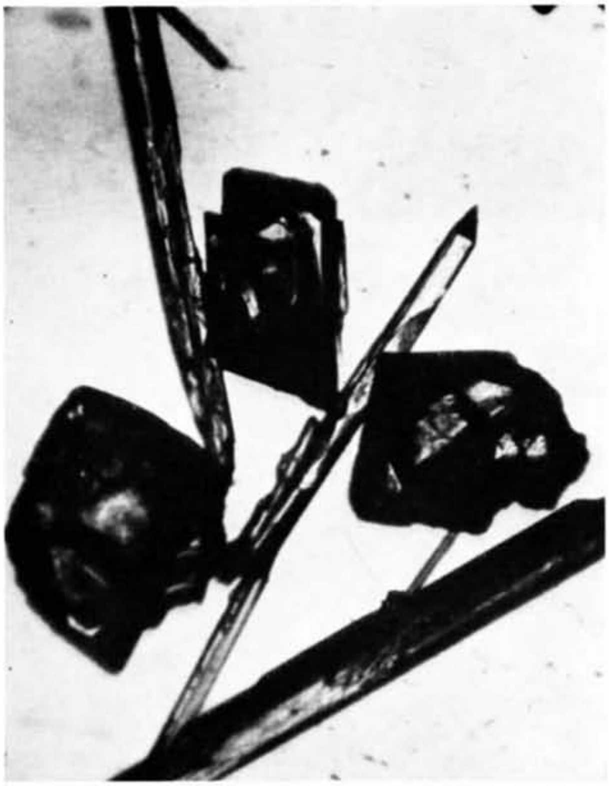
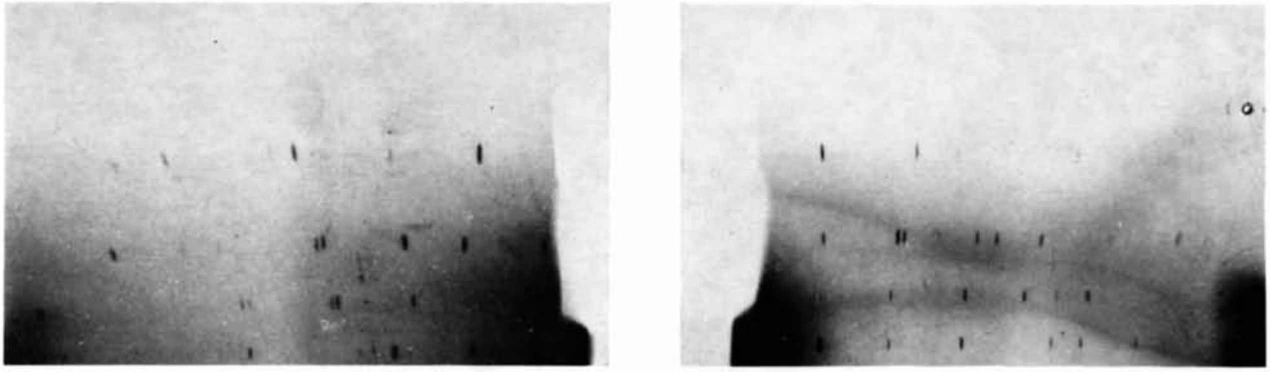
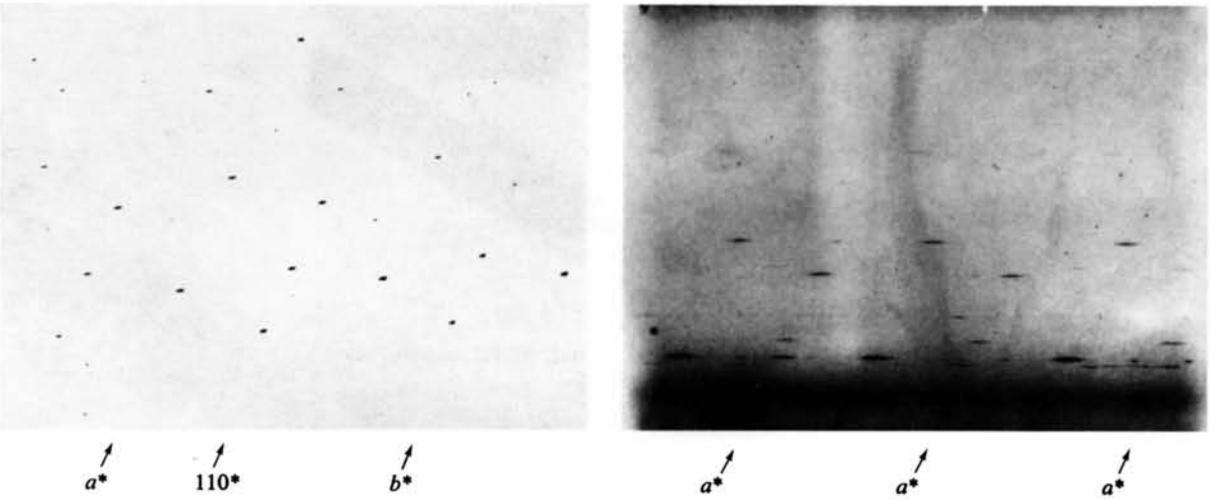


Fig. 1. Micrograph of single crystals of III (needles) and V (prisms).



(*a*) (*b*)

Fig. 2 Oscillation Photographs of III (at RT) and I at 550 K. Rotation axis, *c*. Cu $K\alpha$ radiation.



(*a*) **(*b*)**

Fig. 3. (*hk*0) Weissenberg photographs III at RT and I at 550 K. The row lines are marked.