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Generation of Polytypic Structures by Thermally Induced Expansion of Stacking Faults in a Titanium Sulphide Single Crystal

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Abstract

A titanium sulphide single crystal of pure 4*H* basic structure has been heated to 1093 K (30 K below its preparation temperature). Observations carried out by microscopy and X-ray diffraction show that, in such conditions, polytypic structures appear with periods which are in perfect agreement with what was expected according to a previously suggested formation mechanism

I. Introduction

A formation mechanism for polytypes of non-stoichiometric titanium sulphide has previously been proposed (Legendre, Moret, Tronc & Huber, 1975*b*; Legendre & Huber, 1977). This suggests that such structures are generated by stacking-fault expansion around screw dislocations during solid-state transformations. Numerous proofs of its validity have already been produced.

The structure and morphology of the crystals we had studied at that time coincided, with no exception, with what was expected according to this mechanism.

The resolution of the structures of some new polytypes has allowed us to go further with this interpretation by suggesting the exact nature of the phase transformation producing the polytypes: 2*H* (11) → 8*H* (3212) and 4*H* (22) → 12*H* (321 321) (Legendre & Huber, 1978).

Accordingly, the next step in this work has been an attempt to produce such structural modifications in a selected single crystal of basic structure. Data concerning this study are reported in this paper.

II. Description of the experiment

A 4*H* (22) single crystal of $TiS_{1.7}$, prepared as described previously (Legendre & Huber, 1977), was sealed in an evacuated quartz capillary tube. In order to prevent any appreciable change of stoichiometry in the crystal by the loss of sulphur during heating, the volume of the tube was reduced as far as possible, *i.e.* to roughly 10 times the volume of the crystal.

The microscopic observations show that (Fig. 1*a*), except for a line running perpendicular to the axis in one of its side faces, it is a quite perfect hexagonal prism. Furthermore, X-ray crystallographic analysis reveals that it exists as a pure 4*H* (22) structure.

In order to induce a phase transition in the crystal, the capillary tube was heated at 1093 K (*i.e.* 30 K below the preparation temperature) for 3, 7 and 14 d. After each heating period the crystal was rapidly cooled and observed by microscopy and X-ray diffraction with a convergent-beam camera (Legendre, Moret, Tronc & Huber, 1975*a*).

III. Results and interpretation

After 3 d, no modification in the morphology of the crystal was noticed but diffusion lines in the X-ray

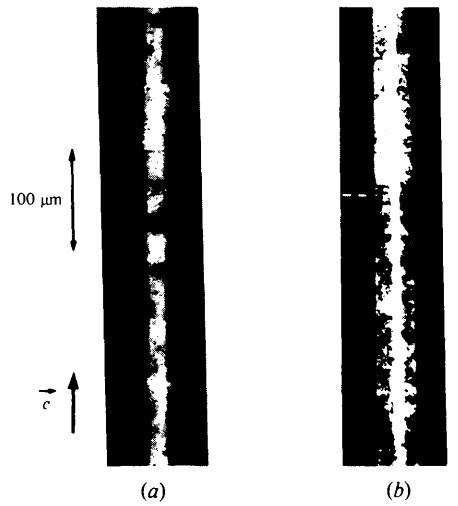

Fig. 1. Photographs of (*a*) one side face of the prismatic crystal before heating, and (*b*) of the same side face after heating for 24 d. Note the lines running at the level indicated by a white dotted line.

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patterns showed that some disorder was induced in the layer stacking sequences by the disordered expansion of stacking faults. An identical behaviour has already been observed in other polytypic compounds.

After heating for 7 d, no perceptible change was observed but after the last period of 14 d (*i.e.* 24 d altogether) some significant changes were seen.

The first change is a modification of the crystal morphology: several lines running perpendicular to the axis in the face which have already been observed (Fig. 1*b*).

It has been noticed previously (Legendre, Moret, Tronc & Huber, 1975*b*) that such morphological discontinuities are related to a polytypic structure formation.

The other changes were noticed on the X-ray convergent-beam pattern. Fig. 2 presents that part of the diagram close to the 202 reflexion of the 4*H* structure.

The 20*l* reciprocal row may be located by the diffusion line it contains. Several diffusion lines (instead of one) can be seen. This phenomenon is produced by the very large magnification of the photograph which reveals strong diffraction on the crystal edges. Because of the diffraction geometry for the 202 reflexion the six edges of the hexagonal prism give only four separated diffusion lines which provide information on the structure of the crystal close to each of these four visible edges.

This separation is possible only because of the good quality of the diffraction patterns obtained by the convergent-beam method.

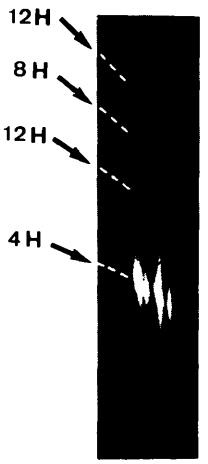

Fig. 2. Enlargement of a diffraction pattern obtained by the convergent-beam method after heating for 24 d. The diffusion lines run along the 20*l* reciprocal row.

Table 1. *Periods of polytypic structures and Burgers-vector lengths of dislocations inducing them during a* $4H \rightarrow 12H$ *phase transformation*

$\lvert\mathbf{V}_B\rvert$	$4d_S$	$8d_S$	$12d_S$
Polytypes	12*R*	8*H*, 24*R*	12*H*

The existence of four diffusion lines shows that stacking disorder is present in most parts of the crystal; however, on these are located extra spots indicating the presence of an 8*H* structure close to two of the edges and of a 12*H* structure (with a very small part of 8*H*) close to another edge of the crystal. The existence of these periods is in perfect agreement with our previous work: if a 4*H* (22) → 12*H* (321 321) phase transformation occurs in a 4*H* (22) crystal, several structures may appear in connexion with the existence of screw dislocations with Burgers vectors of different size.

Table 1 shows the relation previously found in that case between the lengths of the Burgers vectors and the periods of the polytypes they may induce (Legendre & Huber, 1978).

According to this, 8*H* may be induced by an $8d_S$ dislocation (d_S: distance between two sulphur layers) and 12*H* by a $12d_S$ dislocation which are frequent because of their rather short Burgers vectors.

IV. Conclusion

In addition to this latter evidence, this experience proves conclusively that polytypes may appear in titanium sulphide after the crystal formation.

Further, it indicates that in such experimental conditions, several weeks are needed to observe some organization in stacking faults, *i.e.* polytype formation.

A better location of polytypic structures in the crystals would be desirable; in this way more accurate data about stacking-fault expansion could be obtained. Along these lines the use of synchrotron-radiation topography should be very promising.

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