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Investigation of phase transition of natural ZnS minerals by high resolution electron microscopy: reply

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Introduction

Fleet's discussion does not, in my opinion, contain any arguments which invalidate my original paper (Akizuki, 1981). Fleet's comments may be summarized under the following headings, and will be considered in the order given: (1) Layer transposition is the dominant mechanism for the 2H → 3C transformation under upper crustal conditions. (2) The degree of disordering of Pribram wurtzite indicated by the lattice image obtained by Akizuki (1981) is somewhat less than the value reported by Fleet. There are evidently some variations of average structural state both within and between samples. (3) The long-range polytypes appear to have a limited or sporadic distribution in Pribram specimens.

Discussion

1. Fleet (1977) suggested, using Jagodzinski's one parameter growth fault model, that the transformation should occur by the layer transposition mechanism. However, Pandey (1981) analyzed a slightly faulted 2H crystal by X-ray and suggested that "the stacking faults involved in the 2H to 3C transformation in vapor grown ZnS crystals are neither growth faults nor layer displacement faults but are predominantly deformation faults". (Fleet, 1977, used the term layer transposition rather than layer displacement.) Layer transposition occurs by a diffusion of atoms through vacancies in a close-packed layer as Pandey (1981) correctly interpreted. The layer glides with respect to the layers of both sides as a result.

Fleet (1983) suggested that *both* deformation (simple crystal slip) and layer transposition appear to be feasible transformation mechanisms for ZnS, which differs from his original opinion (Fleet, 1977) as he himself described. Unfortunately, Fleet (1977, 1983) has no evidence for layer transposition in ZnS crystals. According to Pandey's X-ray analysis (1981), diffusion controlled layer transposition appears in a transformation of SiC crystals.

According to my observation (Akizuki, 1981) of the crystal lattice of ZnS by high resolution transmission electron microscopy, "it seems that the crystal lattices glide in one of four possible directions according to the strain orientation during heating or cooling". That is, I support Pandey's opinion (1981), though whether layer transposition occurs in ZnS crystals at all is not known.

If layer transposition occurs in ideal 2H (11) structure, the stacking sequence .....112211..... in the Zhdanov notation must be produced. The stacking sequence shown in Figure 6 (Akizuki, 1981) is more complicated ....112313211...., and is by no means evidence for the layer transposition mechanism. The stacking sequence, ...112211... can be accidentally produced from the ideal 2H structure by two simple crystal glidings.

I observed the stacking sequences of acicular ZnS crystals produced by KCl flux and vapor methods. The ZnS crystals produced in KCl flux grew in the range of 1100–1000°C and were kept at 800°C for various times. The ZnS crystals produced from the vapor phase grew in an evacuated silica tube at about 1100°C and cooled slowly. Both crystals showed kinked prism faces, which according to the observation by Mardix and Steinberger (1970), developed due to crystal gliding during cooling or heating. Such crystals consist of a mixture of both ordered and disordered structures. The ordered structure consists of 2H, 3C, and many polytypes, whose lattice images were observed by use of a high resolution transmission electron microscope by the present writer (unpublished). The 2H crystal includes many simple stacking faults, some of which were produced during cooling; the stacking sequences, ...112211... are rarely observed. The degree of disordering (α) of the Pribram specimen is only 0.25, that is, 75 percent of 2H structure is retained by the specimen. Also, the stacking sequence, ...112211.... is hardly observed in this specimen.

A twin gliding occurs commonly in heated sphalerite; the crystal, when heated, prepares itself for the forthcoming transition by thermal deformation twinning (Akizuki, 1970). The thermal deformation twinning is no more than one event in the process of phase transition from the 3C to the 2H structure, following the 4H and other polytypes.

Both wurtzite and sphalerite grow under similar conditions in nature, at least, with respect to growth temperature. Fleet (1977) suggested that wurtzite (2H) transforms into sphalerite (3C), whereas there are no documented examples of 3C → 2H transformation in nature, because the layer transposition by the isolated edge dislocation mechanism can occur only in the 2H structure, while it is impossible in the 3C structure. That is, a process of solid state transformation of ZnS crystals proceeds only in one direction, and as a consequence, becomes a complicating factor in assessing the thermodynamic stability of ZnS

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phases (Fleet, 1977). It is quite in the nature of things that "one-way solid state transformation" occurs at low temperature. Formation of wurtzite and sphalerite is affected mainly by sulphur fugacity (f_S) and temperature (Scott *et al.*, 1972). Wurtzite can grow under low f_S conditions at temperatures even as low as 200°C. According to thermodynamics, sphalerite cannot transform into wurtzite at such a low temperature as 200°C, even if crystal slip occurs as easily in the sphalerite crystal as in graphite and talc, but transforms into wurtzite by simple crystal slip at high temperature (1020°C for pure ZnS).

2. I agree with Fleet's opinion that structural states vary from specimen to specimen.

3. The Pribram specimen I used did not exhibit long-range ordered polytypes such as 65, 100, and 130 layers, though some short range polytypic structures, which were accidentally produced during cooling, showed many fine diffraction maxima on the $10\bar{1}l$ and $20\bar{2}l$ rows (Fig. 4, Akizuki, 1981).

I have observed long-range periodic polytypes such as 114R $[53(33)_5]_3$ in acicular ZnS crystals synthesized from the vapor phase (unpublished) and because I can find no long-range polytypes in the Pribram disordered specimens I cannot believe that there is a possibility that such a polytype exists in them. Only the lattice image can clarify the partially ordered polytype structure in the disordered crystal. I hope that Dr. Fleet is able to show the existence of long-range polytypes in his Pribram specimen by high resolution transmission electron microscopy.

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