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

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Several years ago, following studies of ZnS minerals from Pribram, Czechoslovakia, Thomaston Dam, Connecticut and Austinville, Virginia (Fleet, 1976; 1977a; 1977b), I concluded that in *natural* (low temperature) assemblages; (1) complete transformation of 2H wurtzite to ideal 3C sphalerite appears to involve two distinct steps, a continuous transformation to intermediate disordered {00.1} layer sequences followed by a final discontinuous transformation; and, (2) in marked contrast, solid-state transformation in ideal 3C sphalerite is essentially limited to the formation of deformation twins ({111} twin plane). The recent observations of Akizuki (1981) on Pribram, zone 1 ZnS (Fleet, 1977b) and Hosokura mine sphalerite tend to support these conclusions: the sampled areas of Pribram ZnS investigated by Akizuki consist only of disordered 2H and 3C sequences, and Hosokura mine sphalerite appears to be in the same structural state as Thomaston Dam sphalerite. However, Akizuki claims that the stacking sequences resolved in his high resolution transmission electron microscopy (HRTEM) study preclude the continuous transformation mechanism (layer transposition) I had proposed for disordered wurtzite.

Stacking disorder (stacking faults) in layered structures can arise through: (1) crystal growth; (2) deformation; and (3) layer transposition. Deformation takes place through crystal slip of the close-packed layers. In contrast, layer transposition (or layer displacement, Pandey, 1981) involves lateral diffusion or migration of individual atoms or of groups of atoms. My original use of the term "isolated edge dislocations" in connection with this process is misleading and henceforth I shall use more widely accepted terminology.

Block-faulted structures may be produced by both crystal growth and deformation and, conceivably, periodic and randomly faulted structures may be produced by crystal growth, deformation *or* layer transposition. Therefore some ambiguity in the assignment of stacking fault origin is to be expected, especially when the process giving rise to the stacking faults does not cause deformation of crystal boundaries.

Both deformation and layer transposition appear to be feasible transformation mechanisms for ZnS. It should be emphasized that *both* processes require a higher activation energy for transformation of the 3C structure and therefore both could account for the principal transformation features of ZnS minerals as summarized in the introduction to the present discussion. There are various studies with single crystal fibers and films of ZnS (*e.g.*, Secco D'Aragona *et al.*, 1966; Mardix *et al.*, 1968) which apparently confirm that deformation faults are readily promoted in 2H wurtzite. Also the frequent occurrence of deformation twins in sphalerite (as in the Austinville sphalerite) shows that crystal slip occurs in the 3C structure under upper crustal conditions, although only at the expense of a certain amount of structural disruption. Layer transposition has been invoked for the 2H → 6H transformation in annealed SiC (Pandey, 1981) and it is fully consistent with the observed features and proposed transformation model of the final stage of the 3C → 6H, 4H, *etc.* transformation in annealed SiC (Ogbuji *et al.*, 1981, Fig. 5b).

My preference for layer transposition as the disordering mechanism of natural 2H wurtzite (Fleet, 1977a) was based on energetic considerations. The physical evidence which I gathered, particularly the X-ray diffraction data, could be interpreted equally well on the basis of either random deformation or random layer transposition models. I recognize that my opinion may change as more definitive evidence becomes available. However, I do not believe that the stacking sequences illustrated by Akizuki (1981) are particularly diagnostic of deformation and exclusive of layer transposition. It should be appreciated that once initiated layer transposition, like deformation, will tend to be repeated sequentially in adjacent layers. A partially transformed crystal will have bands of transformed structure within a matrix of the original structure. Isolated transposed layers are less likely. Furthermore, as is indicated by Fleet (1977a, Fig. 1c), little transformation of 2H wurtzite is required to effectively conceal the original matrix structure. Also, contradicting Akizuki's assertion that isolated faults do not occur in his lattice images, we have in Figures 5 and 6 (Akizuki, 1981) the sequence (downwards) of ACACAB̄AC.

It should be admitted that my interpretation of the X-ray diffraction data for Pribram wurtzite (Fleet 1976) has not met with unquestioned acceptance. Pandey (1981) argues that these data were incorrectly analyzed. However, layer transposed disordered 2H stacking sequences

*are* fully consistent with the X-ray diffraction theory used in Fleet (1976) and this may be confirmed qualitatively by structure factor calculations on finite disordered stacking sequences.

The degree of disordering of Pribram, zone 1 wurtzite indicated by the lattice images obtained by Akizuki (0.25) is somewhat less than the value reported by Fleet (1976; 0.325). The latter value is consistent with the maximum birefringence of the crystal used for the X-ray diffraction study and is within the range of values (0.325 to 0.40) found to be representative of zone 1 wurtzite in the sample of Pribram schalenblende investigated by me (Fleet, 1977b). Also, supposed relict areas do exhibit a wide range in degree of disorder (0.0 to 0.25; Fleet, 1977b, Fig. 4). However, this does not imply that Akizuki's value is not representative of the sample investigated by him. There is evidently some variation of average structural state both within and between samples. Similarly, the long-period polytypes reported by Fleet (1975) appear to have a limited or sporadic distribution.

## References

Akizuki, M. (1981) Investigation of phase transition of natural ZnS minerals by high resolution electron microscopy. American Mineralogist, 66, 1006–1012.

Fleet, M. E. (1975) Wurtzite: Long-period polytypes in disordered 2H crystals. Science, 190, 885–886.

Fleet, M. E. (1976) Stacking disorder in natural 2H wurtzite. Journal of Applied Crystallography, 9, 190–192.

Fleet, M. E. (1977a) Structural transitions in natural ZnS. American Mineralogist, 62, 540–546.

Fleet, M. E. (1977b) The birefringence-structural state relation in natural zinc sulfides and its application to a schalenblende from Pribram. Canadian Mineralogist, 15, 303–308.

Mardix, S., Kalman, Z. H., and Steinberger, I. T. (1968) Periodic slip processes and the formation of polytypes in zinc sulfide crystals. Acta Crystallographica, A24, 464–469.

Ogbuji, L. U., Mitchell, T. E., and Heuer, A. H. (1981) The $\beta \rightarrow \alpha$ transformation in polycrystalline SiC: III, The thickening of $\alpha$ plates. Journal of American Ceramic Society, 64, 91–99.

Pandey, D. (1981) X-ray diffraction study of solid state transformations in close-packed structures. Proceedings Indian National Sciences Academy, 47, A, 78–99.

Secco d'Aragona, F., Delavignette, P., and Amelinckx, S. (1966) Direct evidence for the mechanism of the phase transition wurtzite-sphalerite. Physica Status Solidi, 14, K115–L118.