American Mineralogist, Volume 66, pages 1006–1012, 1981

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

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Abstract

Heated sphalerite and natural disordered wurtzite from Pribram, Czechoslovakia have been studied by high resolution electron microscopy. The sphalerite heated at 950°, 1000° and 1050°C commonly shows 2H, 4H and twinned 3C structures with a few 12R and 15R polytypes. The 4H polytype may be stable only in a limited temperature range. ZnS specimens from Pribram consist only of disordered 2H and 3C sequences, no 4H sequences were found. A stacking sequence due to so-called isolated or coupled partial dislocations was not found in either of heated sphalerite or natural wurtzite. The original sphalerite and wurtzite were deformed by local thermal strains at an early stage of the phase transition, and then recrystallized at the final stage, resulting in a considerably ordered structure.

Introduction

Zinc sulfide minerals crystallize in cubic close-packed (sphalerite) and hexagonal close-packed (wurtzite) forms, and their mixtures (polytypes). Hill (1958) suggested that when sphalerite is heated in the temperature range 960° to 1020°C, intergrowths of 3C and 2H and especially 4H polytypes are more stable than either 3C or 2H or a mechanical mixture of them. Akizuki (1970) studied relations between the 3C → 2H phase transition and crystal imperfection of sphalerite. He heated natural sphalerite at 1000° to 1050°C for 1 to 5 minutes with KCl powder that melted at 776°C, and observed many slip lines. These lines were produced by gliding parallel to {111}, on the (110) cleavage plane and the (111) surface. Generally, the crystal gliding is not affected by the original stacking faults, but by local thermal strains. Also, by means of transmission electron microscopy, he found that both translation gliding and twin gliding occur in the heated sphalerite.

The transition temperatures ranging from 600° to above 1240°C reported in some papers (*e.g.*, Scott *et al.*, 1972) are a univariant function of f_{S_2} and temperature. Scott *et al.* (1972) suggested that since wurtzite is thermodynamically more stable at low f_{S_2} than sphalerite, wurtzite can form under low temperature hydrothermal conditions in nature.

Some natural wurtzites consist of a disordered stacking sequence which is a transitional state between 2H and 3C, whereas others are completely transformed into ordered sphalerite 3C. Wurtzite from Pribram, Czechoslovakia has an extremely high degree of stacking disorder, which was observed by transmission electron microscopy (Akizuki, 1970; Fleet 1975). Fleet (1975) reported 20Å fringes in Pribram specimens, that correspond approximately to a 6H period, and reflections corresponding to 65, 100 and 130 layers in the diffraction patterns.

Specimens

Two kinds of sphalerites were collected from the Hosokura mine, Japan: one is fibrous and black, the other is massive and brown. The massive sphalerite (a = 5.40Å), which contains some iron, shows few twins and stacking faults in transmission electron microscope images. The massive sphalerite was heated, in the presence of excess sulfur, in an evacuated silica tube at 930°, 950°, 1000°, 1050° and 1200°C. The specimen heated at 930°C for 2 hours showed no change in the powder X-ray diffraction pattern. When the specimen was heated at the same temperature for 20 hours, a weak and broad peak appeared at d = 3.20Å, though the peaks of original sphalerite hardly changed. In the specimen heated at 950° and 1000°C for 2 hours the intensity of sphalerite peaks decreased and some wurtzite peaks appeared with a peak at d = 3.20Å. The polytype peak decreased in the specimen heated at 1050°C for 2 hours, and dis-

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appeared at 1200°C, with the result that only a wurtzite structure remained. The structure of the polytypes cannot be analyzed on the X-ray diffraction pattern, because they form only a few broad peaks.

The fibrous black colored sphalerite (a = 5.42Å) from the Hosokura mine contains about 20 atom percent of FeS. This fibrous sphalerite forms as a result of the phase transition from an original wurtzite and now consists of polysynthetic rotation twins about [111], though the crystal contains some original sphalerite lamellae (Akizuki, 1969). The spacing of twins ranges from several Ångstroms to about one micrometer.

ZnS minerals from Pribram, Czechoslovakia are composed of parallel growths of two kinds of fibrous crystals: one is pale brownish and isotropic, the other is deep brownish and non-isotropic. The isotropic fibers consist of sphalerite structure with a few stacking faults, while the non-isotropic fiber is composed of a disordered wurtzite structure (Akizuki, 1970).

The purpose of the present study was to observe the process of both 2H→3C and 3C→2H phase transitions by means of high resolution transmission electron microscopy, and to discuss the transition mechanism.

Observations

The crushed grains were observed by high resolution electron microscopes (JEM 100 and JEM 1000). High resolution transmission microscopy has become a powerful method in the study of polytypes, especially irregular stacking sequences. A one to one correspondence between structural features analyzed by an electron diffraction pattern and lattice image was established by observations of common short-periodic ZnS polytypes, 2H, 3C and 4H.

The 3C→2H phase transition

Massive sphalerite from the Hosokura mine was used for the study. For specimens heated at 930°C stacking faults and twin boundaries parallel to (111) showed little increase in the specimen heated for 2 hours, while they increased in abundance considerably in the specimen heated for 20 hours.

Specimens heated at 950°, 1000° and 1050°C showed distinct changes which consisted of 2H, 4H, 12R, 15R and polysynthetically twinned 3C structures. Some twins repeated at the spacing of several unit cells (Fig. 1), though others have intervals of about one thousand Ångstroms (Akizuki, 1970). Figure 2 shows the 4H polytype intergrowth with 3C layers. The 2H structure was not observed in these samples. The 4H is the commonest polytype, with widths greater than 20 unit cells, whereas 12R $(31)_3$ and 15R $(32)_3$ polytypes are scarce and their widths are less than several unit cells (Fig. 3). The sphalerite heated at 1200°C transformed into a relatively ordered 2H structure without any intergrown polytypes, and showed the distinct diffraction maximum of the 2H structure (Akizuki, 1970).

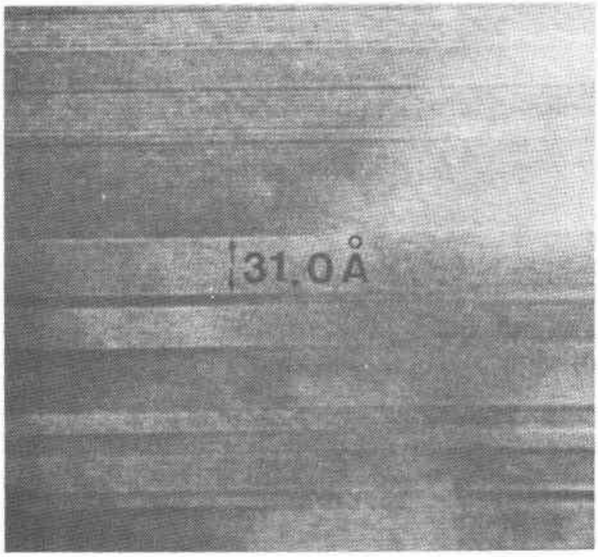

Fig. 1. Lattice image showing thermal deformation twins of sphalerite heated at 950°C. The glide and twin planes (111) are horizontal, and the (110) plane is parallel to the photograph. The distance 31.0Å corresponds to the thickness of ten layers.

The 2H → 3C phase transition

Pribram specimens are principally composed of 2H structures, though 3C layers are observed (Fig. 4). Some difficulties are encountered in analyzing the disordered stacking sequence of ZnS by means of the lattice image, because of the small differences between A, B and C positions on the image. The polytypic stacking sequences can be denoted by a plus sign (+) and a minus sign (−) of Hägg notation. A structure ABCABC. . . . is thus represented as + + + + ... , while the structure CBACBA . . . . is denoted by − − − − . . . . . . , and the structure ABAB . . . . . is represented by + − + − + − . . . . . . In Figures 4 and 5, the sequences of the minus signs are shown by white dotted lines, whereas those of the plus signs are shown by the black lines. Therefore, one can easily analyze the stacking sequence on these photographs. The areas of alternate white dotted lines and black lines correspond to 2H structure (+ −

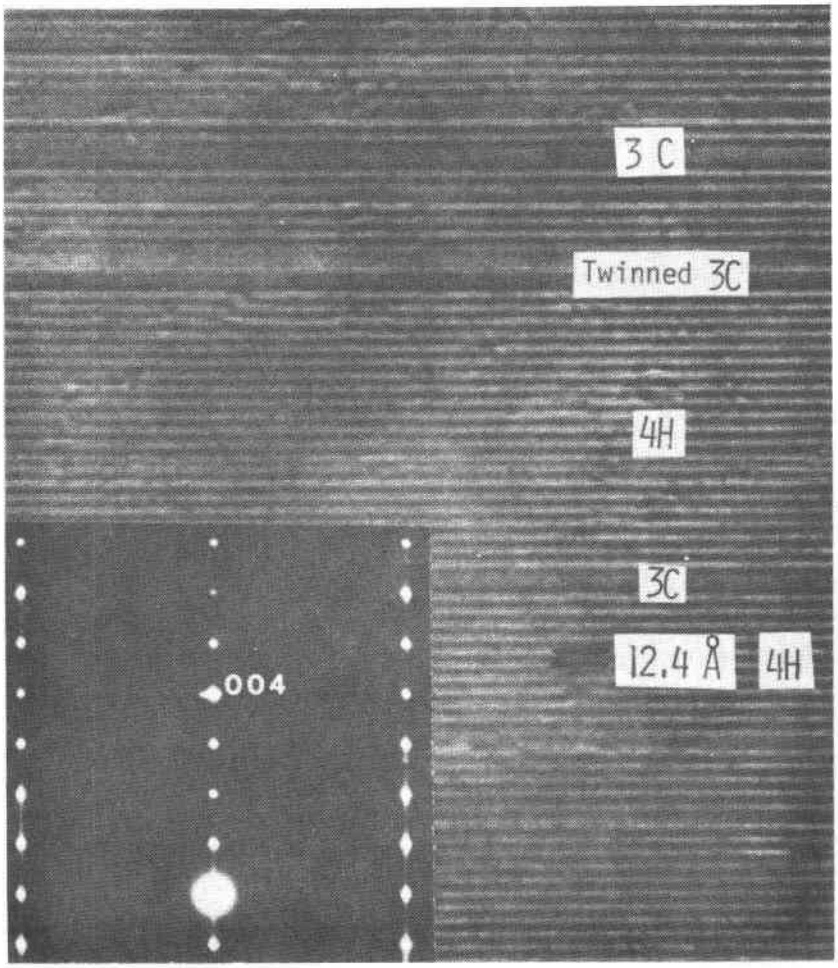

Fig. 2. Lattice image showing the 4H polytypes with the 3C lamellae in the sphalerite heated at 950°C. The stacking plane is horizontal and the (11$\bar{2}$0) plane is parallel to the photograph. The diffraction pattern was taken from a larger area including the lattice image shown here.

+ − . . . .) (6.2Å in Figs. 4 and 5), and the bands consisting of inclined white lines or black bands are composed of twin related 3C structure (Fig. 4), which can be shown by + + + + ... or − − − − . . . .

The degree of disordering (a), which is directly calculated from the photographs, is about 0.25, corresponding to one stacking fault in every four layers of wurtzite structure. Fleet (1977) calculated the a-value of the specimen from the same locality using the Jagozinski method, and showed $a = 0.325$, which is higher than the present value. Also, Fleet (1977) reported 20Å fringes, approximately equal to a 6H period, with widths comprising 65, 100 and 130 layers found from measurement of the diffraction patterns. The present specimen, however, did not exhibit these long range ordered polytypes, though some short range polytypic sequences, which were accidentally produced during cooling, show many fine diffraction maxima on 10$\bar{1}l$ and 20$\bar{2}l$ rows (Fig. 4).

Some areas of dark contrast, which contain partial edge dislocations with Burger's vectors parallel to the stacking plane, are shown by arrows in Figure 5. A complex stacking mistake is shown in the area enclosed by the brackets, and is shown schematically in Figure 6. This sequence may be formed from an original 2H structure which contains two stacking faults by two additional translation glidings as follows:

BABA|CACACACA|CBCBCBC
↓
BCBCBC|BABABAB
↓
AB|ACACACA
BABA|CA|BCBC|AB|ACACACA

The vertical lines show stacking faults. It is highly probable that original crystals contained many stacking faults and their structure was complicated by later gliding.

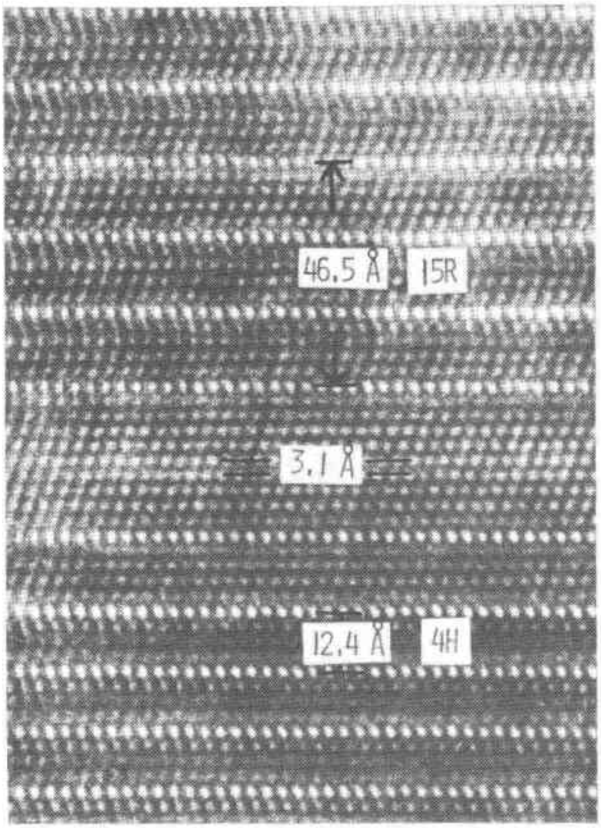

Fig. 3. Lattice image showing the 3C, 4H and 15R structures in the sphalerite heated at 950°C. The orientation is the same as shown in Fig. 2. Short range polytypic sequence (1131) is shown.

Fibrous sphalerite from the Hosokura mine consists of polysynthetic twins of ordered 3C structure with a few disordered 3C structures. The space between the twin planes ranges from a few unit cells to about one micrometer.

Discussion

The 3C → 2H phase transition

Figure 7 shows stacking sequences of short range polytypes and their stacking direction. For instance, the arrow of 15R polytype indicates the direction connecting both ends of the ABCACB sequence. Also, the degrees (Q) of inclination of stacking direction of the *c* axis are shown on the figure. In 15R $(32)_3$ with a zig-zag sequence, the Q value is calculated to be $(3-2)/(3+2) = 0.2$. The Q values are 0 for 2H (11) and 1 for 3C (30) structures, and those of polytypes are between 0 and 1.

In the 3C structure, gliding can occur along one of the four {111} planes by heating, and stacking faults and twins are produced just below the transition temperature (Akizuki, 1970). Gliding continues until the slip planes meet with other (111) slip planes, thus the crystal is divided into many blocks. The orientation of gliding in each block is not affected by pre-existing stacking faults, dislocations, or other defects, but is determined by local thermal stresses (Akizuki, 1970).

According to the degree of thermal strain, sphalerite will transform into short-period polytypes just below the phase transition temperature, the temperature at which the crystal lattice can easily glide. This mechanism is similar to that of optical twinning in microcline (Akizuki, 1973), though the twinning mechanism is not lattice translational in orthoclase→ microcline. The orientation of strain in original orthoclase determines the type of transition twinning in microcline, *i.e.*, albite or pericline twinning. The opti-

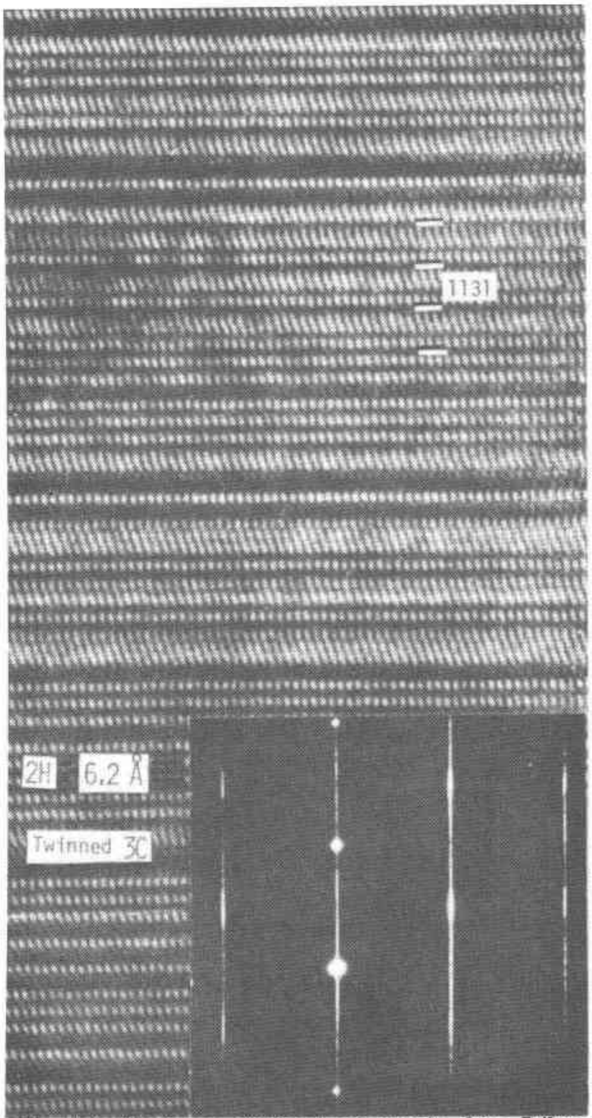

Fig. 4. Lattice image of disordered wurtzite from Pribram, Czechoslovakia. The orientation is the same as that of Fig. 2.

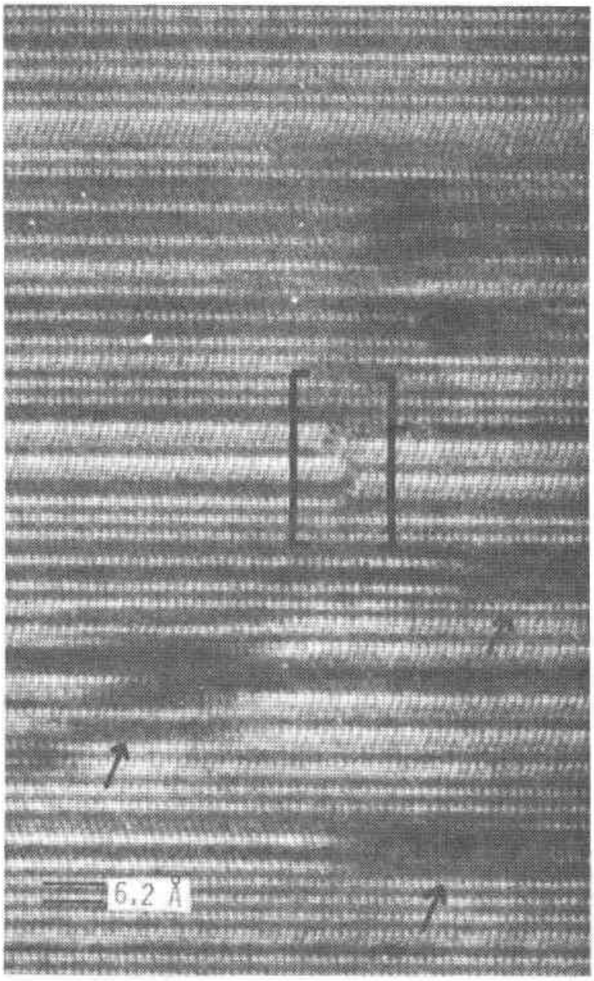

Fig. 5. Lattice image of disordered wurtzite from Pribram, Czechoslovakia. The orientation is the same as that in Fig. 2. (See details in text.)

cal twin lamella in microcline is composed of abundant sub-microscopic twins (Akizuki, 1972). Depending on the direction and degree of strain, the volume ratio of A and B components in M-twins will differ in every optical twin band. When the strain is negligible in the original orthoclase, the ratio A/B is 1 and the microcline is optically monoclinic. The greater the strain, the larger or smaller the ratio A/B, and the boundary at which the ratio is 1 corresponds to the optical twin boundary. The ratio A/B is nearly constant in the optically homogeneous strain field (Akizuki, 1973).

The stacking sequence of the polytype, which is an intermediate state of transition from 3C to 2H, will follow the degree of strain in sphalerite during heating. The greater the strain the more stable the polytype with a lower Q value. The 15R polytype (Q = 0.2) will be produced in an area with higher strain than that of the 12R polytype (Q = 0.5). Since the thermal-induced strain field is not homogeneous in the sphalerite, 15R and 12R polytype layers are narrow, consequently long-period polytypes will not be produced in the heated sphalerite.

A similar phenomenon is observed in a melt-grown ZnS crystal. ZnS crystals grown from the melt phase at 1200°C and 60 kg/cm^2 are composed of fine polysynthetic 3C twinnings repeated at every three, four or five layers (Akizuki, unpublished). The melt grown 2H crystal transforms very quickly to 3C during cooling (Ebina *et al.*, 1967). The change in external crystal shape due to lattice translation is constrained by the crucible to be small, resulting in repeated twinnings.

It may assumed that the 4H polytype is produced by stronger strains than those necessary for 12R and 15R polytypes. The 4H polytype, however, is observed to be much more abundant than 12R and 15R polytypes, and therefore the 4H polytype may be thermodynamically more stable in a limited temperature range during heating.

Although Fleet (1977) proposed a so-called couple partial dislocation mechanism for the 3C → 2H

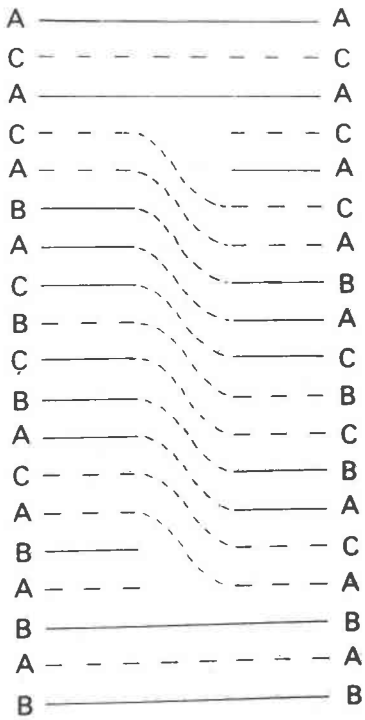

Fig. 6. Stacking sequence in the bracket shown in Fig. 5. Distinct white contrasts as shown by straight lines and absent images (black lines) are shown by dashed lines.

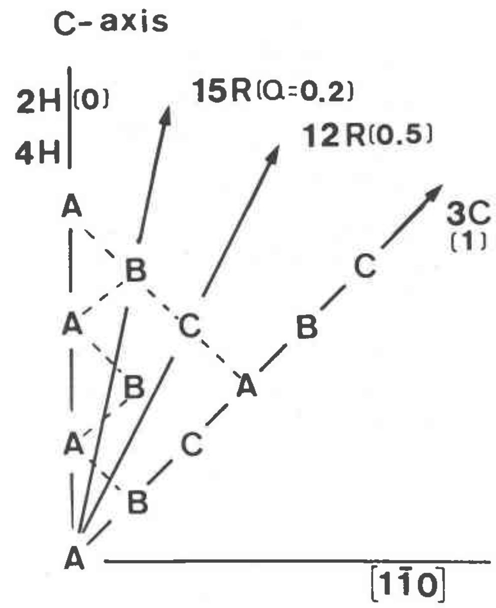

Fig. 7. Stacking sequence and direction of ZnS short range polytypes. (See details in text.)

phase transition, the stacking sequences due to this mechanism were not found in the heated sphalerite. Sphalerite is deformed by the local thermal strain at an early stage of phase transition.

The 2H → 3C phase transition

Fleet (1976) discussed three possibilities to account for different types of stacking faults: (a) growth, (b) unit edge dislocation movement involving individual layers during the phase transition, or (c) deformation, and suggested that the disordered sequences in the Pribram wurtzite is due to either growth or edge dislocation movement, but there is no means to distinguish between the two mechanisms. However, Akizuki (1970) and Fleet (1977) assumed the Pribram specimen to be in the process of phase transition. Akizuki (1970) suggested that polysynthetically twinned fibrous sphalerite from the Hosokura mine transformed from well-ordered wurtzite, because regular hexagonal growth hillocks were found on the tip of the fibers using a replica method under the electron microscope. Thus, it may be assumed that the disordered ZnS crystal from Pribram must be in the process of transforming to the 3C structure as well.

Fleet (1977) proposed an isolated partial edge dislocation mechanism in order to explain the 2H→3C phase transition in ZnS. According to this mechanism, the layer above transposed one snap back, and the ABABABAB sequence changes into ABACA BAB. This sequence, however, cannot be found in several photographs showing the lattice images. It seems that the crystal lattices glide in one of four possible directions according to the strain orientation during cooling.

The Pribram specimens are composed of only 2H and 3C structures, and no other polytypes are found. Also, Fleet (1976) suggested that a continuous variation in structural state does not exist between ordered 2H and ordered 3C, since a phase of the latter invariably develops within a 2H matrix in the Pribram specimen. Fleet's observation is pertinent to the case of the Pribram specimen. However, the 4H polytype is common in the heated sphalerite.

Why are the phase transition processes not reversible between the two kinds of specimens? The transition temperature of the two specimens are different: one is 1000°C and the other, the Pribram specimen is about 200°C. Dislocations are easily initiated on the surface or the grain boundary at high temperature, and therefore the crystal lattice can glide successively in the heated specimen, resulting in a metastable 4H polytype. Also, short range polytypes such as 12R and 15R are produced by local thermal strain. However, the initiation of a dislocation is difficult at low temperature, and each layer parallel to (0001) of the original Pribram crystal does not always contain dislocations. Therefore, the lattice of the Pribram specimen cannot glide successively, resulting in disordered structure. Thus, the Pribram specimen did not form the 4H polytype or the short range polytypes, but transformed through the disordered structure into the 3C structure. Some partial dislocations are found in Pribram wurtzite (Fig. 5), while they are rarely observed in the heated sphalerite. The crystal gliding is easy at high temperature and the glide dislocation can quickly arrive at the crystal edge.

The disordered crystal is recrystallized at the final stage of transformation (Fleet, 1977). Polysynthetic twinned fibrous sphalerite from the Hosokura mine, whose twin components are much thicker than those of Pribram specimen, may be the result of the recrystallization of disordered or ordered 2H structure at the stable condition of 3C structure.

Thus, depending on the direction and degree of strain, the phase transition of ZnS occurs by gliding in one of four possible directions during cooling or heating, following recrystallization.

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Manuscript received, October 30, 1980;
accepted for publication, April 29, 1981.