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SLIP STRUCTURE OF HEATED SPHALERITE

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ABSTRACT

The purpose of this study is to investigate detailed relations between the $3C \rightarrow 2H$ phase transition and crystal imperfections of sphalerite. Many stacking faults and dislocations were detected by etching. The sphalerite crystals were heated at 1000 to 1050°C for 1 to 5 minutes with KCl powder that melted at 776°C. Many slip lines, produced by gliding on $\{111\}$, were observed on (110) cleavage planes and (111) of heated sphalerite. Generally, slip lines were not affected by the stacking faults, although some slip lines were interrupted by close-spaced stacking faults. The structure of heated sphalerite with many slip lines was studied using X-ray and electron diffraction, and it was found that translation gliding and twin gliding occurred on heating. Thus heated sphalerite prepares itself with twins and stacking faults for the forthcoming transition.

INTRODUCTION

Zinc sulfide minerals crystallize in the form of close-packed structures: cubic close-packed (sphalerite), hexagonal close-packed (wurtzite), and their mixture (polytypes). It is well known that wurtzite changes to disordered wurtzite through geologic times (Jagodzinski, 1949), and is finally transformed into polysynthetically twinned sphalerite. The present writer found that fibrous sphalerite from the Hosokura mine, Japan has hexagonal growth patterns on (111), and the crystals are transformed completely into polysynthetically-twinned sphalerite (Akizuki, 1969). Recently, Daniels (1966) and Mardix *et al.* (1968) discussed needle-like wurtzite, grown by the vapor-phase method, that transformed into sphalerite and some polytypes by the layer transposition mechanism of Jagodzinski (1949).

The $3C \rightarrow 2H$ phase transition of ZnS is assumed to occur at 1020°C. Hill (1958) suggested that in the temperature range 960 to 1020°C, an intergrowth of $3C$ and $2H$ crystals is more stable than either of these polymorphs or a mechanical mixture of them. Akizuki (1968) has observed by electron microscopy many fine streaks of some polytypes, twins of sphalerite, and stacking faults in thin films of heated sphalerite.

The purpose of this study is to investigate details of the $3C \rightarrow 2H$ phase transition of ZnS using optical microscopy and an electron microscope with an electron accelerating potential of 100kV. In order to define relations between crystal gliding and crystal imperfection, the writer used optically anomalous sphalerite, and compared it with sphalerite that did not show optical anomalies.

SPECIMENS

Sphalerite specimens used in this study were taken from the vein-type deposit of the Hozawa mine, Japan. The sphalerite occurs as brown-colored euhedral crystals, about 5 cm in diameter. The 220 reflection of X-ray powder patterns is broad, but 111 is sharp. A thin film parallel to the (110) cleavage plane was made by the cleavage replica method (Akizuki, 1967), and was examined by electron microscopy (Fig. 1A). A number of striations were observed to cross the crystals from one edge to the other, whereas some were very short. Similar features were seen in synthetic zinc sulfide platelets by electron microscopy (Chadderton *et al.*, 1963, 1964; Fitzgerald *et al.*, 1967). These evidently represent defects which lie on (111) planes perpendicular to the photograph. Although Mitchell and Corey (1954) point out that

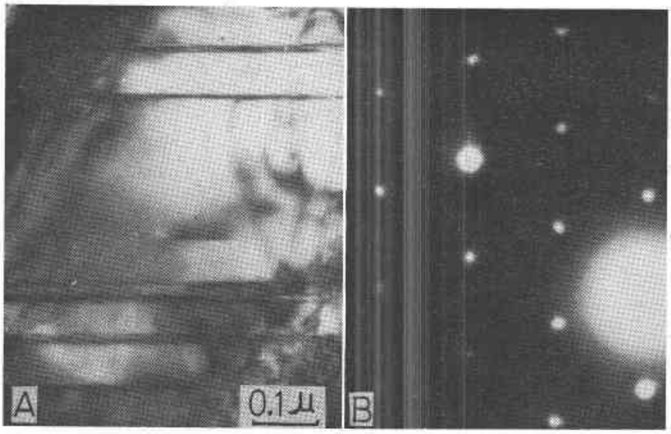

FIG. 1. Electron micrograph showing: (A) stacking faults and (B) the electron diffraction pattern of (110) thin film of sphalerite.

preparation conditions often favor an intergrowth of sphalerite and wurtzite, the striations are considered to be a simple stacking defect. Diffraction patterns (Fig. 1B) taken from areas shown in Figure 1A show a streaking of spots in the [111]* direction. Stacking faults in this sphalerite are more numerous than in that from other localities (Akizuki, 1968). Also, many dislocations were found in the present material.

Optical Anomaly and Etch Figures

Under the polarizing microscope with crossed nicols, two kinds of optical anomaly were observed in (110) cleavage platelets. One type is a sharp line with diffused anomalous bands on both sides (Fig. 2A), elongate in the [$1\bar{1}0$] direction on the (110) plane. The other is a cloudy type. This sphalerite shows stronger birefringence than sphalerite from other localities.

Dislocations and stacking faults in the crystals were observed by the

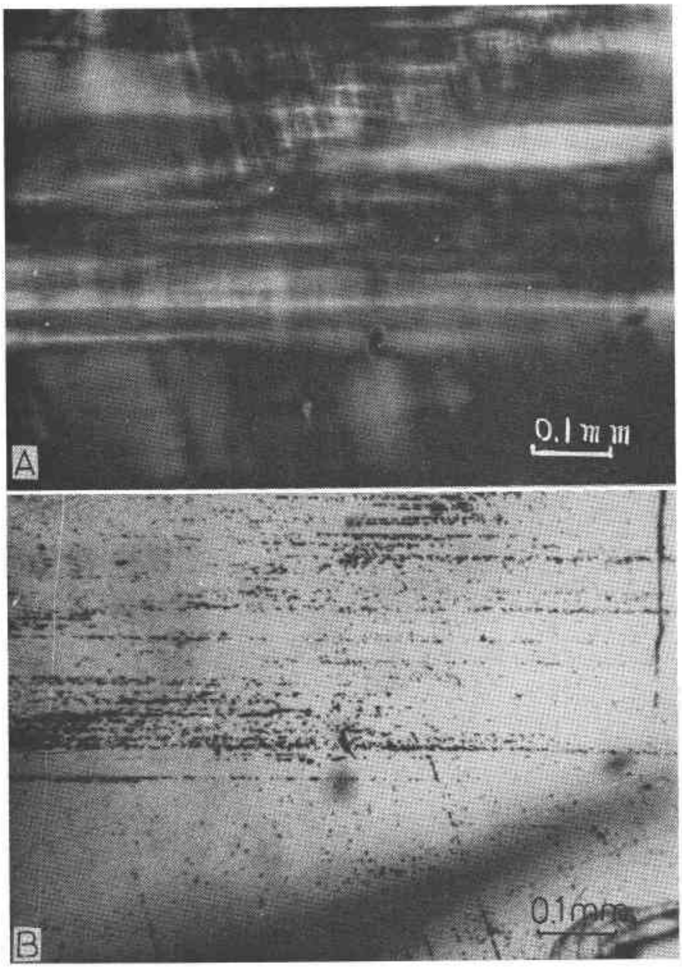

FIG. 2. Optical micrographs showing (A) optical anomalies in (110) section and (B) etch pits on these optical anomalies.

etching method, and were compared with optical anomalies. These crystals were cleaved by the usual method along (110) planes, and freshly cleaved faces were etched in 30 percent H_2O_2 at 80°C for 10 to 20 minutes. As fine crystals of ZnO formed on the etched plane, an acetyl cellulose film was pasted with acetone solution on this plane; after drying it was stripped, thereby removing the fine ZnO crystals. The cleaned (110) planes were observed under optical and electron microscopes. Many rough striations parallel to [001] on (110) were observed by optical microscopy. Examination of such surfaces highly magnified by electron microscopy showed that fine, close striations parallel to $[1\bar{1}0]$ covered the surfaces and intersected the rough striations. Many etch pits and etch lines on which the rows of etch pits are situated run parallel to $[1\bar{1}0]$. Examples are given in Figure 2B. Both the etch pits and etch lines show one-to-one correspondence in number and position on matched faces. This feature suggests that they may be dislocation pits and stacking faults. Results of more precise examination will be reported later.

Sphalerite included other crystals during crystal growth or exsolution. The crystals are optically anomalous in a cross-like pattern around these

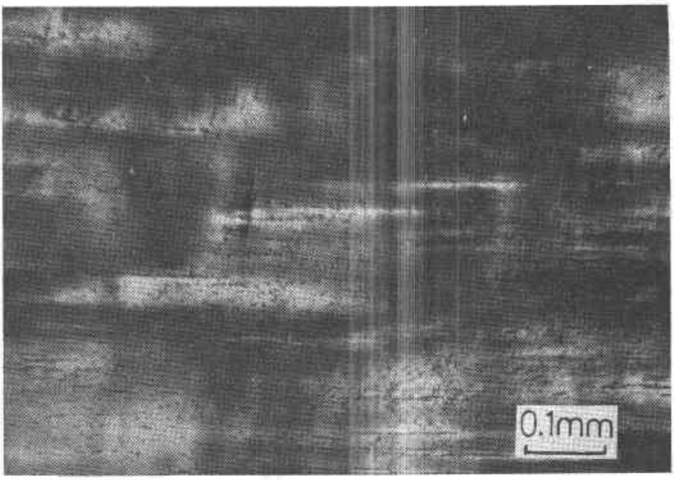

FIG. 3. Optical micrograph showing optical anomalies with many impurities in (110) section.

inclusions. Small impurities situated on the stacking faults (Fig. 3) caused stronger birefringence. Stacking faults decorated by impurities can be observed under the microscope even with no nicol prism at all.

When the optically anomalous crystal was heavily etched, etch lines with many etch pits were found on the sharply anomalous line (Fig. 2B). Frequently the optical anomaly formed a grid pattern, and the etch features followed this grid. Crystals showing a cloudy type of optical anomaly are covered with randomly distributed small etch pits. Specimens without a strong optical anomaly have only a few etch pits or stacking faults.

The (111) growth surface of sphalerite crystals was studied previously with optical and electron microscopy by Votava *et al.* (1953), Verma (1956), and Komatzu and Sunagawa (1965); growth trigons, growth layers, slip lines, and etch pits were observed on the faces. The specimens used for the present study were naturally etched; etch trigons and etch grooves were found on (111) faces. Etch grooves on the (111) plane are parallel to $[10\bar{1}]$ and connect with the etch lines on (110) cleavage planes.

Slip Lines in Heated Sphalerite

Sphalerite crystals were heated with KCl powder at 1000 to 1050°C for 1 to 5 minutes. KCl powder melts at 776°C; this molten KCl prevents deformation and oxidation of sphalerite, and etches the stacking faults. The heated specimens were cooled in air and washed with water. The

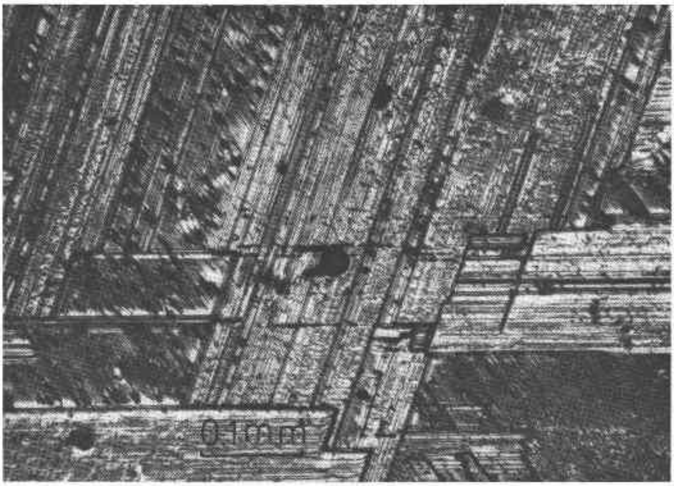

Fig. 4. Optical micrograph showing slip patterns on (110) of sphalerite heated at 1000°C for 2 minutes.

(110) and (111) planes were then examined under the optical microscope, and complex linear patterns were found. Figure 4 shows a typical (110) plane; the lines parallel to $[1\bar{1}0]$, $[1\bar{1}2]$ and $[11\bar{2}]$ are slip lines produced by gliding on $\{111\}$. The plane is separated into many blocks; slip lines in each block are parallel with one another. Some blocks show an irregular boundary, but in most cases the boundary is straight and parallel to a single slip line. Although the stacking faults in unheated sphalerite were seen to cross each other and produced a grid-like optical anomaly (Fig. 2A), in many cases the slip lines made by heating did not cross each other, except that a few protruded from the boundary between blocks (Fig. 4).

A sphalerite crystal was cleaved in two parts, and both crystals were heated in molten KCl at the same time. The correspondence of slip patterns on these matched planes was examined under the optical micro-

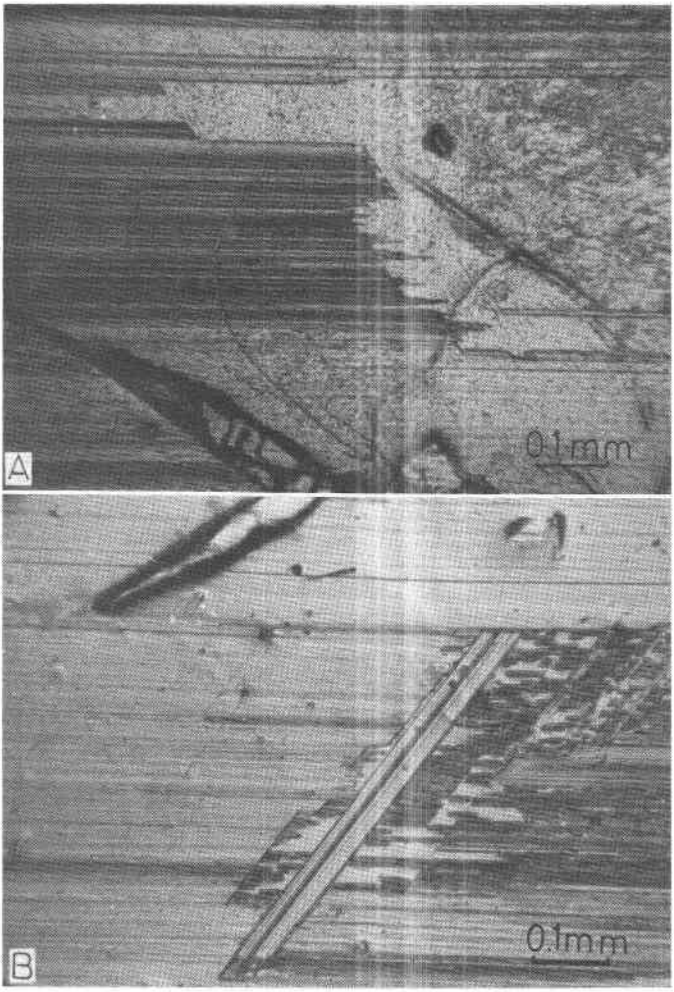

FIG. 5. Optical micrographs of slip patterns on matched (110) planes of sphalerite heated at 1000°C for 2 minutes.

scope. Generally, the slip patterns on the matched planes were different, though in some cases they were similar. Figures 5A and 5B show a somewhat simpler linear pattern, which is similar in both crystals. Generally, slip lines were not affected by the original stacking faults in the starting material, although some slip lines were interrupted by close-spaced stacking faults or were parallel to them (Figs. 5A and 5B). Also, Figures 5A and 5B show the difference in amount of gliding on the opposite sides. Etch lines of the original stacking faults in heated sphalerite

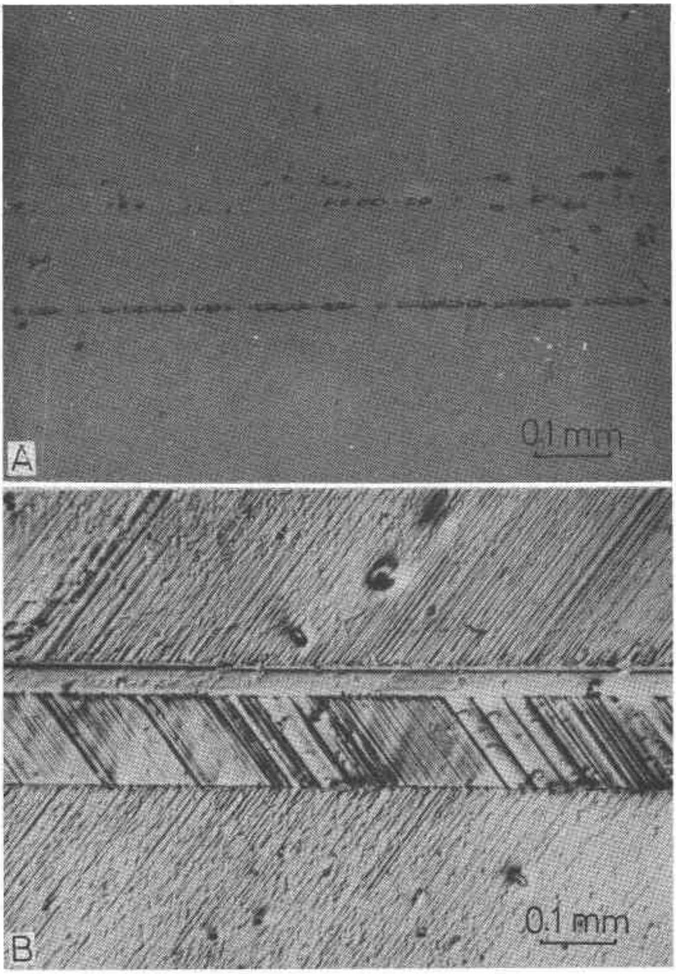

FIG. 6. Optical micrographs of etch figures on (110) of (A) unheated sphalerite with twins and (B) their slip pattern after heating.

did not always correspond in position and amount, although the stacking faults in unheated sphalerite did show such a correspondence.

Figure 6A shows twinned sphalerite, the twin plane being {111} (*i.e.*, spinel-type twinning). The orientation of etch striations changes in twinned regions, and optical microscopic twins are easily distinguished from stacking faults. Figure 6B shows slip lines that change their orientations at the twin boundary. Other specimens, however, showed slip lines parallel to the twin boundary.

Figure 7 shows slip lines on the (111) face. These were produced by gliding on {111} planes inclined to the micrograph. Regions giving wavy patterns from molten KCl etching may be parallel to the slip plane.

From the present work it is concluded that small stacking faults, dislocations, and other defects in unheated sphalerite do not affect the orientation of gliding. Gliding continues until the slip plane meets with other slip planes and the crystal is divided into many blocks. The orientation of gliding in each block may be determined by local thermal stresses.

Sphalerite without a strong optical anomaly showed the same results as the optically anomalous crystals.

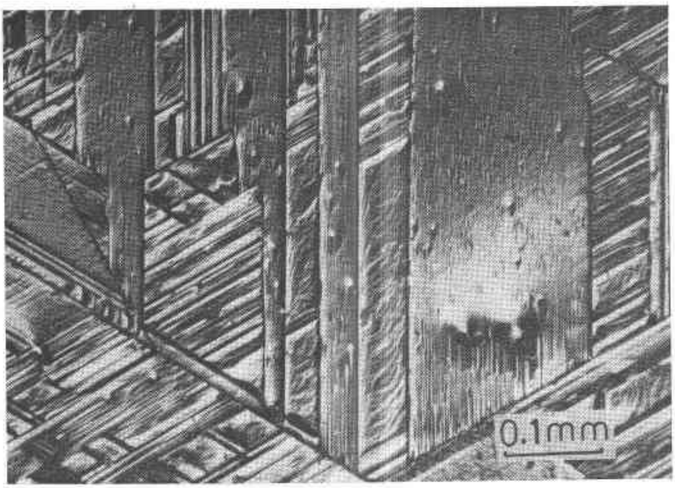

Fig. 7. Optical micrograph showing slip pattern on (111) of sphalerite heated at 1000°C for 2 minutes.

Crystal Structure of Heated Sphalerite

The crystal structure of heated specimens with many slip lines was obtained from X-ray powder patterns and electron diffraction patterns. Some wurtzite was found on the X-ray patterns of sphalerite crystals heated at 1050°C for 5 minutes. Specimens heated at 1000°C for 1 to 2 minutes, however, have no wurtzite, and their X-ray powder patterns were the same as unheated sphalerite. When (110) thin films of heated specimens without wurtzite were observed directly under the electron microscope, many striations were found to cross the crystals from one edge to the other (Figs. 8A and 8C). Their electron diffraction patterns show spinel twins (Fig. 8B) and stacking disorder (Fig. 8D) of sphalerite.

According to classical theory, plastic deformation of crystals can oc-

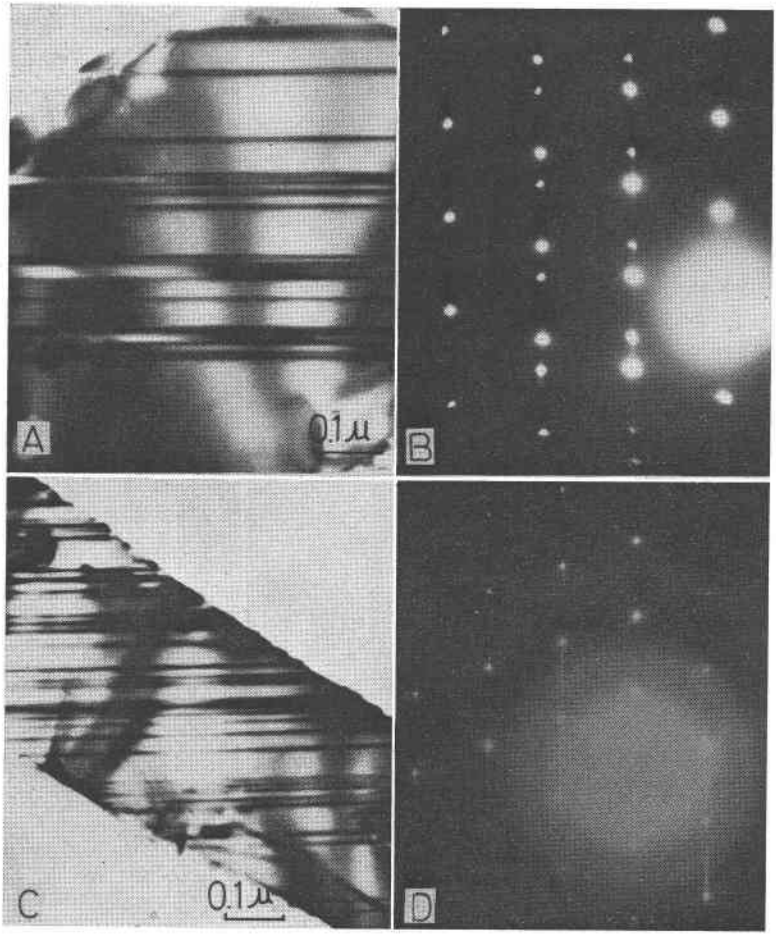

FIG. 8. Electron micrographs and corresponding electron diffraction patterns of (110) thin films of sphalerite heated at 1000°C for 2 minutes: (A and B) show twinning and (C and D) show stacking disorder.

cur either by slipping or twinning. Buerger (1928) concluded that sphalerite deforms by movement along {111} planes, and that the character of the movement is that of twinning rather than translation. He also suggested that a very pure crystal would be expected to deform by translation while an impure one, having distorted planes upon which extensive slip would be attended by great friction, would be expected to deform by twinning. Translation gliding and/or twin gliding is expected to occur in sphalerite by heating. Figures 8C and 8D show that stacking faults in a sphalerite film and attendant streaks in its diffraction pattern

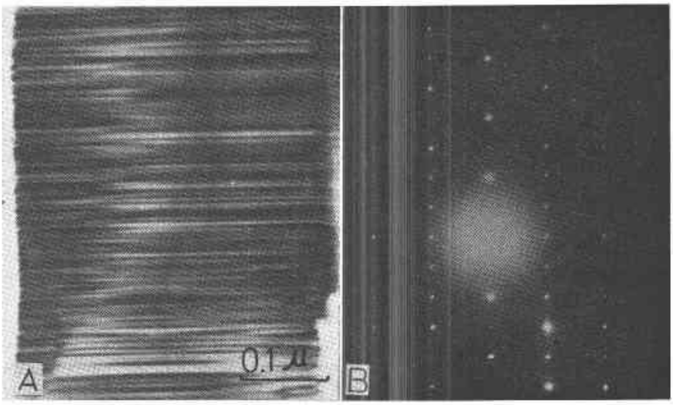

FIG. 9. Electron micrograph and electron diffraction pattern of wurtzite transformed from sphalerite by heating at 1200°C for 2 hours.

are formed by translation gliding. Figures 8A and 8B show that twin gliding occurs in sphalerite by heating; the crystal, when heated, prepares itself for the forthcoming transition by thermal deformation twinning. Recent studies by Young (1962) and Sadanaga and Sueno (1967) on the α–β transition of quartz and Ag_2S have presented examples of twin formation as a phenomenon presaging a transition. When sphalerite twinning is repeated within a short range, the resulting structure approaches that of wurtzite. As the temperature rises, sphalerite twinning increases, and finally sphalerite changes to wurtzite containing many stacking faults. An example is shown in Figures 9A and 9B.

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