

THE BIREFRINGENCE - STRUCTURAL STATE RELATION IN NATURAL ZINC SULFIDES AND ITS APPLICATION TO A SCHALENBLENDE FROM PRIBRAM

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ABSTRACT

Birefringence increases nearly linearly with percent hexagonal close-packed layers in natural zinc sulfide, and this correlation is used to estimate the variation in structural state within a zoned schalenblende from Příbram, Czechoslovakia. Collectively, the various zones exhibit an almost complete variation in structural state of disordered wurtzite and sphalerite. The present study supports earlier suggestions that the wurtzite \rightarrow sphalerite inversion in nature proceeds in two steps, a second-order solid-state transformation to disordered hexagonal zinc sulfide followed by recrystallization via a fluid phase.

SOMMAIRE

La biréfringence augmente presque linéairement avec le pourcentage de feuillets en empilement hexagonal compact dans le sulfure de zinc naturel. Cette corrélation est employée ici pour évaluer la variation de structure dans une schalenblende zonée provenant de Příbram, Tchécoslovaquie. Considérées collectivement, les différentes zones montrent un éventail presque complet de structure de wurtzite et de sphalérite désordonnées. Cette étude confirme des hypothèses précédentes à l'effet que l'inversion wurtzite \rightarrow sphalérite dans la nature se produit en deux étapes, à savoir une transformation du deuxième ordre à l'état solide en un sulfure de zinc hexagonal et désordonné suivie d'une recristallisation impliquant une phase liquide.

(Traduit par la Rédaction)

INTRODUCTION

The crystal structures of zinc sulfide minerals are all based on stacking sequences of a common unit — a close-packed layer of Zn-S dipoles, indicated (below) by *A*, *B* or *C*. Wurtzite has the hexagonal close-packed *2H* sequence *ABABAB* . . . , stacked along the *c* axis, and sphalerite has the cubic close-packed *3C* sequence *ABCABCAB* . . . , stacked along [111] directions. An infinite variety of stacking sequences between these ideal *2H* and *3C* end-member structures is possible. More than 150 ordered intermediate structures (polytypes) have been reported (Steinberger *et*

al. 1973). Some degree of stacking disorder is very common and completely disordered structures have also been reported (for example Fleet 1975, 1976).

Although the inversion temperature for sphalerite \rightleftharpoons wurtzite is near 1020°C at 1 atm (Allen & Crenshaw 1912), the equilibrium for this reaction seems to be a univariant function of $f(S_2)$ (Scott & Barnes 1972) and sphalerite and wurtzite may coexist over a wide temperature range. An overall understanding of the stability of zinc sulfide phases is complicated by such factors as (1) the existence of ordered and disordered intermediate structures, (2) the reaction-path dependence of solid-state transformations (for example, Baars & Brandt 1973), (3) the common occurrence of natural wurtzite, the high-temperature modification, in low-temperature environments, and (4) the widespread instability of wurtzite relative to disordered hexagonal zinc sulfide and sphalerite under post-formation conditions.

Natural wurtzite assemblages frequently contain zinc sulfide in several structural states. In the present study, the variation in birefringence and chemical composition within a schalenblende specimen from Příbram, Czechoslovakia is investigated in some detail. The near-linear relation between birefringence and percent hexagonal close-packed layers is developed, and use is made of it to deduce the variation in structural state within the hand specimen. Previous studies of zinc sulfides from this hand specimen have dealt with the resolution of stacking faults in disordered *2H* wurtzite (recognized as zone 1 wurtzite in the following section) by transmission electron microscopy (Fleet 1975), and X-ray determination of the degree of stacking disorder in zone 1 and zone 7 wurtzite (Fleet 1976).

PETROGRAPHY

The schalenblende sample (8×5×3 cm in size) was obtained from the Mineralogical Museum, University of Cambridge, where it was catalogued as wurtzite, No. 384. It is capped by a

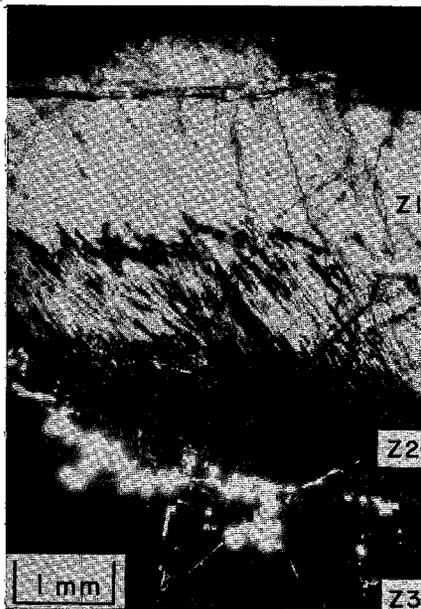
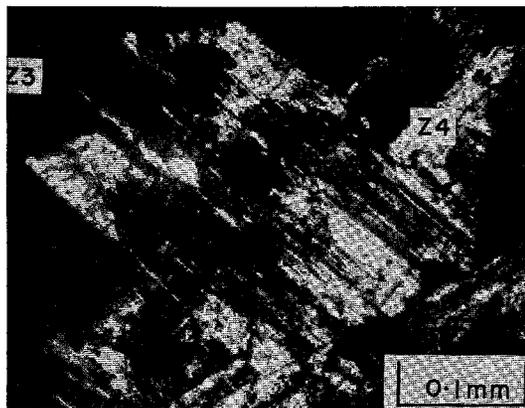


FIG. 1. (top): photomicrograph of Pribram schalenblende showing zone 4 zinc sulfide (Z4) with large grain, euhedral against zone 3 galena (Z3), containing ragged (00.1) lamellae and bands of disordered wurtzite and sphalerite (crossed nicols).

FIG. 2. Photomicrograph of Pribram schalenblende showing zone 1 wurtzite (Z1), zone 2 sphalerite (Z2), and zone 3 galena (Z3) (crossed nicols).

sheaf of radiating $\{00.1\}$ and $\{00.\bar{1}\}$ plates or blades of brown wurtzite. Detailed hand-specimen and thin-section observations lead to the recognition of seven distinct layered zones which were evidently deposited in a vein or cavity wall. The wurtzite capping the hand specimen (zone 1 below), represents the final phase of crystallization which extended into the fluid phase. The complete sequence of zones is:

1. orange to light brown bladed wurtzite. 3 to 5 mm thick.
2. pale yellow sphalerite. 1 to 2 mm thick.
3. galena band partly encrusted with quartz. 4 mm thick.
4. yellow hexagonal zinc sulfide/sphalerite crystals, euhedral toward the galena band and encrusted on zones 5 and 6 (Fig. 1). 0.1 to 0.3 mm thick.
5. (a) lenticular patches of colorless to pale yellow sphalerite with deep red rims adjacent to zone 4. 0.2 to 0.6 mm thick;
(b) sphalerite similar to 5a except more ovoid or rounded in outline and located within zone 6.
6. red-brown and brown sphalerite. 5 mm thick.
7. (a) hexagonal zinc sulfide with sphalerite as sporadic encrustations on siderite-quartz matrix adjacent to zone 6 and on small masses of sphalerite, similar in appearance to that of zone 6, within siderite-quartz matrix;
(b) aggregates of hexagonal zinc sulfide crystals within siderite-quartz matrix, often as either encrustations or cavity linings.

Colors refer to appearance in thin sections of standard thickness. The wurtzite of zone 1 is pleochroic with maximum absorption normal to the c axis. Adjacent to the contact with zone 2 sphalerite it contains fine striations which are much more markedly pleochroic than the matrix and may represent strained (00.1) dislocation slip planes. The contact between zones 1 and 2 is very irregular. Zone 2 sphalerite extends into zone 1 wurtzite as ragged lamellae and contains discontinuous fragments of bladed wurtzite grains (Fig. 2). Furthermore, grain boundaries, identical to those of the bladed wurtzite grains of zone 1, extend continuously through zone 2. The relation of zone 5 to zone 6 is unclear, but the texture suggests formation through either solution-reprecipitation or replacement processes. Much of the sphalerite in this schalenblende contains anisotropic areas and the birefringence of the hexagonal zinc sulfide varies markedly throughout the specimen.

BIREFRINGENCE OF THE PRIBRAM ZINC SULFIDE

The accepted value for the birefringence of $2H$ wurtzite is 0.024 (Brafman & Steinberger 1966; Nelkowski & Pfitzen-Reuter 1971). Brafman & Steinberger, working on ordered polytypic regions within structurally complex synthetic zinc sulfide, established that birefringence is a linear function of percent ZnS layers in hexagonal close-packing (σ) and discounted an earlier report to the contrary (Singer 1963). The pola-

rizability tensors of the hexagonal and cubic zinc sulfide environments must differ only slightly so that the birefringence of any intermediate stacking sequence is a resultant of the contributions of the individual hexagonal and cubic close-packed layers. This condition holds regardless of the manner in which the hexagonal and cubic close-packed layers are stacked (structurally distinct polytypes with the same σ value will have identical birefringence) and regardless of whether a stacking sequence is ordered (polytypic) or disordered. Nelkowski & Pfitzen-Reuter (1971) substantiated the results of Brafman & Steinberger. However, their data, which were taken largely on disordered synthetic stacking sequences, show only an approximately linear relation between birefringence and σ ; birefringence is somewhat less than the ideal value (Fig. 3).

The correlation between birefringence and σ has been established on pure synthetic zinc sulfide, but it should be possible to apply it to natural zinc sulfide, that is, to estimate the structural state of an optically coherent zinc sulfide region from its birefringence. The only potentially limiting factor is the effect of atomic substitution. Data are not available to make a systematic evaluation of this, but Hurlbut's (1957) study suggests that birefringence is virtually independent of Cd substitution. In separate stu-

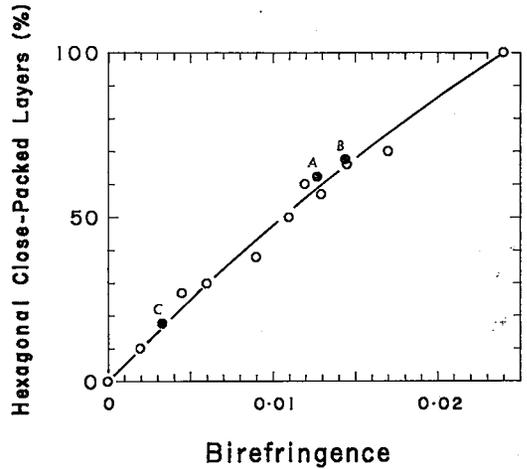


FIG. 3. Comparison of percent hexagonal close-packed layers (σ) and birefringence ($n_x - n_y$) for synthetic (and principally disordered) zinc sulfide (open circles, Nelkowski & Pfitzen-Reuter 1971) and for natural zinc sulfide (full circles). A and B are disordered 2H wurtzite from Příbram and C is disordered 3C sphalerite from Thomaston Dam.

dies (Fleet 1976, 1977), the σ values of three natural disordered zinc sulfide crystals were determined by analysis of the observed X-ray scat-

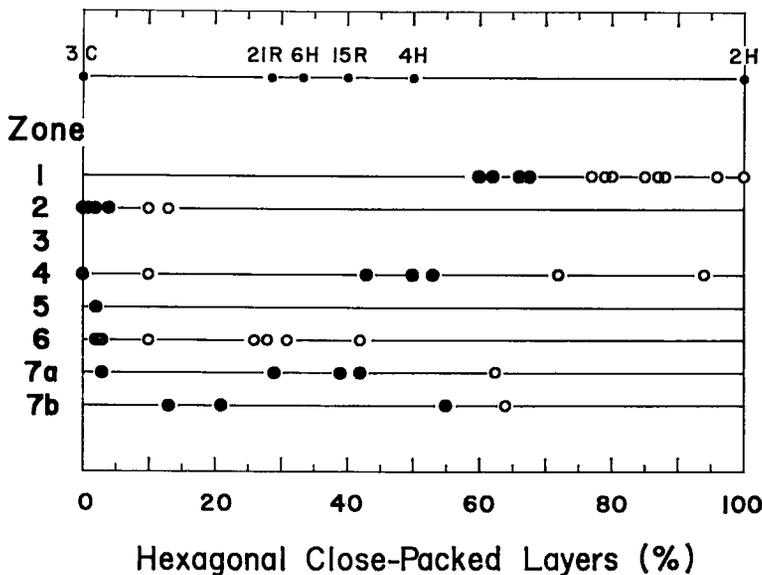


FIG. 4. Percent hexagonal close-packed layers (σ) in representative areas within each of the six zinc sulfide zones of the Příbram schalenblende (full circles); non-representative areas are shown as open circles. Data for ideal polytypes are included for comparison. σ is estimated from Figure 3 and, hence, is proportional to birefringence.

tering on the 10/1 reciprocal lattice row. The maximum birefringence of these crystals has since been determined and these data are included in Figure 3. Retardation (Δ) was measured with a Berek compensator (No. 3270. E. Leitz, Wetzlar, West Germany) with the crystals oriented both on a spindle stage and mounted in oil on a glass plate; crystal thickness was measured using a microscope at 75 \times magnification with a calibrated eye-piece micrometer and with the crystals oriented on a spindle stage. Crystals A and B are both disordered 2H wurtzite from Pribram: A is from zone 7a, and B is from zone 1. Also measured was an additional crystal (C in Fig. 3), which is a disordered sphalerite from Thomaston Dam, Connecticut. The data for crystals A, B and C (Fig. 3) are consistent with those for the synthetic disordered crystals of Nelkowski & Pfützten-Reuter and these data, taken collectively, define a polynomial rather than linear relation between birefringence and σ .

Birefringence determinations have been made on a variety of grains from the zinc sulfide zones in the Pribram hand specimen. Several thin sections were used in the study. Grain thicknesses were obtained either by estimation from the maximum birefringence of nearby quartz, or by direct measurement on neighboring grains removed from the thin sections. These data, converted to equivalent percent hexagonal close-packed layers using the smoothed calibration curve of Figure 3, are summarized in Figure 4. The thin sections were cut normal to the plane of the wurtzite blades of zone 1 so that the grains in zones 1 and 2 were oriented to give maximum birefringence. In zones 4, 5 and 7, measurements were taken only on lamellae with sharp edges, giving maximum birefringence. However, there may be a slight tendency for the resulting σ data to err on the low side, since it was difficult to estimate the exact orientation of the grains in these zones; this error, if it exists, has no effect on the conclusions drawn from this study. The data in Figure 4 are fully representative of the variation in birefringence (and structural state) within each of the zones recognized in the Pribram hand specimen but, of course, measurements were not made on all of the appropriately oriented birefringent areas in each thin section.

The wurtzite of zone 1 appears in thin section as lamellae, about 50 to 200 μm in width, which wedge-out against each other as they pass toward zone 2. The birefringence of most of this wurtzite is uniform (about 0.014, equivalent to σ in the range 60 to 68%). There are, however, a few discontinuous lamellar areas, 5 to 10 μm in width, with higher birefringence: the maxi-

mum birefringences measured are 0.024 and 0.0247, both in good agreement with the expected value for ideal 2H wurtzite. Much of the zone 2 sphalerite is weakly birefringent (less than 0.001), detailed examination showing the sphalerite grains to be a diffuse, patchy, anisotropic mosaic under crossed polars.

Most of the zone 4 zinc sulfide is composed of ragged and discontinuous lamellae of hexagonal zinc sulfide and sphalerite (Fig. 2). The hexagonal zinc sulfide is only slightly less uniform in birefringence than the zone 1 wurtzite (about 0.011; $\sigma=50\%$) and like the latter, it has lamellar and lensoid areas of higher birefringence.

The zone 5 sphalerite is weakly birefringent, the grains showing a diffuse patchy anisotropy. A few clear areas are isotropic. The zone 6 sphalerite contains many lamellar fragments of higher birefringence, arranged in an apparently random manner, and the matrix has a diffuse patchy anisotropy. The zone 7 hexagonal zinc sulfide consists of platy crystals, 100 μm or so in width, which are banded with lamellar strips of different birefringence. The observed variation in birefringence is approximately from 0.002 to 0.013. The sphalerite areas within this zone resemble the zone 6 sphalerite.

ELECTRON MICROPROBE ANALYSIS

Electron microprobe analyses were made at the Department of Mineralogy and Petrology, University of Cambridge, using a Geoscan operated at 20 kV, and calibrated as follows: Zn and S (in zinc sulfide) with pure synthetic ZnS; Fe and S (in pyrite) with a natural pure pyrite; Cd with pure synthetic CdS; Cu with pure metallic Cu; Mn with pure metallic Mn; Ca with pure calcite; Mg with olivine (29.66 wt. % Mg). Matrix corrections were made with program T.I.M.I. Forty-eight individual spot analyses were made on the Pribram zinc sulfide (each spot was counted in triplicate): Fe ranged between 0.8% and 2.2%, Cd between 0.1% and 1.4%, Cu from not detected to 0.10%, Mn from not detected to 0.08%, and S between 32.1% and 32.6%. The total weight percent elements is consistently less than 100% (~98-99%), and subsequent analyses on the MAC 400 microprobe in the author's Department realized similar discrepancies. The raw count data for Zn and S are both less than the corresponding data for the ZnS standard, and it seems likely that X-ray excitation or emission in the zinc sulfide sample was reduced by some physical factor, perhaps poor conductivity.

DISCUSSION

X-ray diffraction studies of several single crystals of hexagonal zinc sulfide from zones 1 and 7 have indicated only disordered $2H$ wurtzite (plus incoherent $3C$ sphalerite) and it seems probable that *all* of the hexagonal zinc sulfide in the Pribram schalenblende is disordered $2H$ wurtzite or a derivative of it. Thus the various zones in the hand specimen, considered collectively (Fig. 4), exhibit a very wide range in structural state of disordered $2H$ wurtzite. In fact, the areas with low percent hexagonal close-packed layers in zone 7b would be described as disordered $3C$ sphalerite and probably have a similar structural state to the Thomaston Dam sphalerite (Fleet 1977). Much of the Pribram sphalerite has a diffuse, patchy anisotropy, and for convenience in representation in Figure 4 the measured birefringence has been converted to percent hexagonal close-packed layers using the calibration curve of Figure 3. However, stacking faults, such as those observed in hexagonal zinc sulfide, are not expected in ideal $3C$ sphalerite (Fleet 1977) and this anisotropy is probably related to localized strain effects.

Ehrenberg (1931) demonstrated that much of the sphalerite associated with wurtzite in schalenblende appears to have developed from earlier wurtzite. The textural relations in zones 1, 2 and 4 are consistent with this interpretation. Although the sphalerite and hexagonal zinc sulfide could have been deposited sequentially, such composite zinc sulfide crystals should display either well-defined (00.1) lamellae or regular concentric growth zones and not the ragged interfaces illustrated in Figures 1 and 2. Also, zone 2 sphalerite is clearly a pseudomorph of earlier hexagonal zinc sulfide. Furthermore, since the lamellar areas within the hexagonal zinc sulfide are often terminated by transverse stacking faults, the lensoid ordered $2H$ areas do have a markedly relic appearance (they are bordered by areas of progressively decreasing percent hexagonal close-packed layers), it does appear that the disordered hexagonal zinc sulfide formed by solid-state transformation of primary $2H$ wurtzite. The rate and extent of this transformation clearly varied markedly, even within individual crystals. However, the textural and structural-state evidence from the Pribram zinc sulfide endorses an earlier suggestion (Fleet 1976, 1977) that the $2H \rightarrow 3C$ inversion in nature proceeds in two steps, a second-order solid-state transformation followed by recrystallization via a fluid phase. The factors which determine the point at which the final recrystallization step is initiated are not well-

understood. Curiously, however, this structural state moves to lower percent hexagonal close-packed layers in passing toward the older zones (Fig. 4).

This study has clearly established the usefulness of maximum birefringence in surveying the variation in structural state in natural zinc sulfide assemblages. Some caution is called for in the application of this technique, however, in that birefringence merely indicates the percent hexagonal close-packed layers and complementary X-ray diffraction studies are required to check for the presence of polytypes. An X-ray powder technique for the *overall* percent hexagonal close-packed layers in a zinc sulfide sample has long been established (Smith 1955). Smith's data for Pribram zinc sulfide (8 and 40 percent) are not inconsistent with the present study, but they are very obviously average values for the material analyzed and, as such, conceal much useful information. It is strongly recommended that complementary petrographic studies be made in using the X-ray powder technique.

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