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ANISOTROPIC SPHALERITE OF THE ELMWOOD–GORDONSVILLE DEPOSITS, TENNESSEE

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ABSTRACT

Sphalerite, the dominant ore-mineral in the Elmwood–Gordonsville Mississippi-Valley-type deposits in central Tennessee, exhibits a distinct anisotropy between crossed nicols. This anisotropy results from the presence of small domains of hexagonal symmetry in the normal cubic structure of sphalerite. These domains result from primary growth-defects that are probably stabilized by local higher concentrations of cadmium and iron.

Keywords: sphalerite, anisotropy, wurtzite, cadmium, Elmwood–Gordonsville, Tennessee.

SOMMAIRE

La sphalérite, principal minéral du minerai des gîtes Elmwood–Gordonsville (Tennessee central) du type dit "Mississippi Valley", est nettement anisotropique entre nicols croisés. Cette anisotropie est due à la présence de petits domaines de symétrie hexagonale dans la structure (cubique) de la sphalérite. Ces domaines résultent de défauts de croissance primaires, probablement stabilisés par la teneur localement plus élevée en cadmium et en fer.

(Traduit par la Rédaction)

Mots-clés: sphalérite, anisotropie, wurtzite, cadmium, Elmwood–Gordonsville, Tennessee.

INTRODUCTION

Sphalerite is the dominant (and commonly the only) ore-mineral extracted from carbonate-hosted (Mississippi-Valley-type) zinc deposits. The sphalerite of the Elmwood–Gordonsville mines in the Central Tennessee zinc district is distinctive in appearance, both megascopically and microscopically. It occurs as very coarsely crystalline, deep brownish, resinous masses that are invariably, and often strongly, anisotropic between crossed nicols in transmitted light. Anisotropy in sphalerite has been attributed to the presence of nonisometric domains. The origin of these domains has been attributed to the partial inversion of wurtzite, the high-temperature polymorph, to sphalerite (Fleet 1977a,b), mechanical deformation (Fleet 1977b), thermal stress (Akizuki 1970, 1981), and contamination of sphalerite by impurities that stabilize a hexagonal structure (Geilikman 1982). In this paper, we describe the characteristics of these specimens, the conditions of their origin, and the investigation of their anisotropy by means of optical studies of doubly polished thin sections and by X-ray-diffraction methods.

GEOLOGICAL SETTING AND PARAGENESIS

The Elmwood–Gordonsville Mississippi-Valley-type deposits, located in the Central Tennessee zinc district, occur in the Lower Ordovician Mascot Formation, associated with paleokarst topography in dolomites (Kyle 1976, Kearns & Campbell 1978, Gaylord & Briskey 1983). Structurally, these deposits lie on the northeastern flank of the gently deformed Nashville Dome (Fig. 1). The mineralization occurs as infillings of massive breccia and vugs and consists of coarse-grained sphalerite with minor amounts of galena, pyrite and marcasite. The gangue minerals consist of calcite, fluorite and strontium-bearing barite, with lesser amounts of quartz, dolomite, celestite and anglesite (Kyle 1976, Kearns & Campbell 1978, Gaylord & Briskey 1983).

Data collected from an examination of doubly polished thin sections and hand specimens suggest a paragenetic sequence dominated by several generations of sphalerite and calcite deposition. The composite paragenetic sequence in Figure 2 attempts to reconcile the observations of Kyle (1976) and Kearns & Campbell (1978) with those of the present study. An important addition is our recognition of two distinct episodes of sphalerite deposition (described below and shown in Fig. 3).

SAMPLES AND METHODS OF INVESTIGATION

Eighteen typical samples of ore from the Elmwood–Gordonsville deposits were kindly provided for this study by Dr. Fred Main of the Jersey Minière Zinc Company. The samples consist of massive coarse-grained sphalerite. Some samples are attached to host dolomite, and others are overgrown by minor amounts of calcite and purple fluorite. Several samples consist of clusters of interpenetrat-

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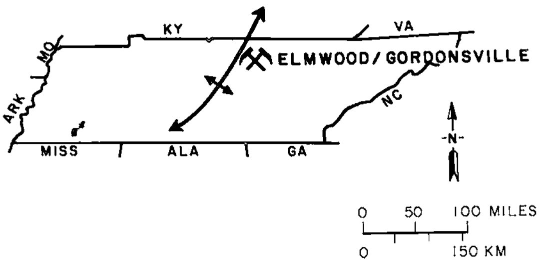

FIG. 1. Location map for the Elmwood–Gordonsville deposits along the northeast flank of the Nashville Dome in central Tennessee.

ing crystals of sphalerite that protrude into open vugs. Coarsely ground surfaces reveal that the massive sphalerite consists of angular to subparallel lamellar single crystals that range from 1 to 3 centimetres in length. Doubly polished thin sections of all samples were prepared in the manner described by Craig & Vaughan (1981), so that examination by both transmitted and reflected light could be conducted.

The composition of selected samples was determined by electron-microprobe analysis on an ARL–SEMQ electron microprobe using synthetic binary sulfide and pure metal standards. Measurements of the unit-cell parameters were carried out on an automated Norelco diffractometer using Ni-filtered Cu$K\alpha$ radiation and CaF_2 as an internal standard. The 133, 024 and 224 reflections were used to calculate cell dimensions. Single-crystal-precession photographs were obtained using a Huber precession camera with Ni-filtered Cu$K\alpha$ and Zr-filtered Mo$K\alpha$ radiation.

Reflectance was measured on a McCrone MPA-1 photometer calibrated against pyrite, galena and magnetite standards which, in turn, had been calibrated against Zeiss WTiC reflectance standard No. 47–42–53. The Vickers microhardness was measured on a Tukon microhardness tester with a 100 g weight and a contact time of 20 to 25 seconds. Fluid-inclusion studies were carried out using a gas-flow stage modified from the design of Werre *et al.* (1979). Sphalerite birefringence was calculated from retardation estimated from a doubly polished thin section mounted on a universal stage. To obtain these estimates of retardation, the thin section was rotated on a univeral stage to the point that gave the maximum retardation. The birefringence was then calculated by taking a visual estimate of the highest-order interference color (the retardation) in conjunction with a thin section thickness that was trigonometrically corrected for the amount of rotation on the universal stage. These data were then applied to an interference-color chart as found in Bloss (1961).

PETROGRAPHY

The Elmwood–Gordonsville deposits have millimetre-sized quartz euhedra present as a discontinuous thin coating around fragments of dolomitic breccia. Dolomite occurs both before and after sphalerite precipitation but only consitutes a minor portion of the gangue minerals (Kyle 1976). Calcite has been recognized in three generations, one before and two after sphalerite formation (Kyle 1976, Kearns & Campbell 1978). Calcite in open vugs may occur as white to slightly yellowish scalenohedral crystals up to tens of centimetres in length. Purple fluorite follows sphalerite and crystallized in cubes up to 10 centimetres across. Strontium-bearing barite appears as roughly hemispherical porous white crystalline masses up to several centimetres across that rest on sphalerite, calcite and fluorite crystals. The rare galena is interpreted by Kearns & Campbell (1978) as forming before sphalerite, but Kyle (1976) stated that it postdates the sphalerite. Pyrite occurs before the sphalerite mineralization in the interstices of car-

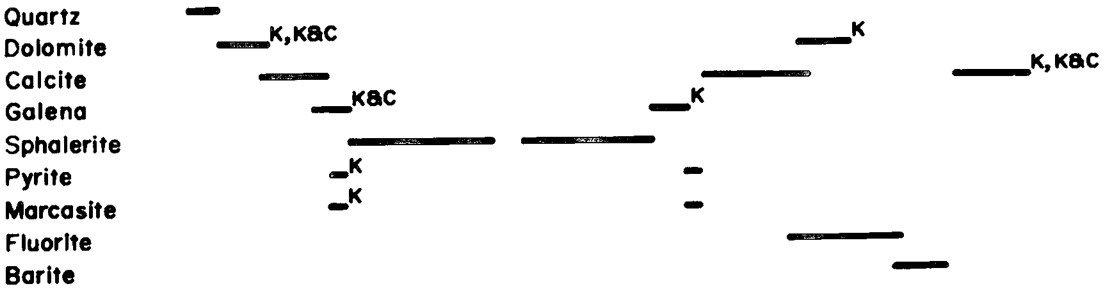

FIG. 2. Composite paragenetic sequence. Note the two distinct episodes of sphalerite deposition. K: observations of Kyle (1976); K&C: observations of Kearns & Campbell (1978).

bonate grains in breccia fragments and as a fracture-filling in second-generation sphalerite. Marcasite is found at the contact between second-generation sphalerite and fluorite. The sphalerite occurs as coarsely crystalline infillings in fractures and between angular fragments of the host carbonates in the breccia. Vugs are lined with myriads of centimetre-sized sphalerite crystals. The sphalerite is generally dark reddish brown but ranges locally to a pale yellowish orange.

Doubly polished thin sections of sphalerite appear a homogeneous grey in plane-polarized reflected light and reveal no observable bireflectance; however, internal reflections are abundant. In plane-polarized transmitted light, two generations of sphalerite can be recognized (Fig. 3). Both generations are clear to light orange in color and display mottled variations in color. Both also locally exhibit subtle growth-banding. The older generation is slightly paler and contains abundant carbonaceous inclusions (Fig. 3) that are totally lacking in the younger generation. These inclusions, which appear megascopically as sharply bounded black laths and rods, are seen at high magnification to be aggregates of small, sometimes diffuse, black, apparently amorphous carbon.

Between crossed nicols in transmitted light, both generations exhibit a distinct anisotropy, generally of low retardation, in thin sections slightly thicker than 0.3 mm. Anisotropic textures range from randomly distributed gridiron textures (Fig. 4) similar in appearance to those found in microcline to textures similar in appearance to polysynthetic twinning (Fig. 5) commonly found in plagioclase. These textures extend apparently undisturbed across the contacts between first- and second-generation sphalerite. and thus either formed continuously because of an initial growth-defect or were superimposed after the second generation of sphalerite had formed.

Sphalerite birefringence calculated from retardations estimated from doubly polished thin sections average 0.002(1) on a universal stage. Birefringence of small domains reaches a maximum of 0.008(2).

EXPERIMENTAL RESULTS

The unit-cell parameter was measured on 14 samples of first- and second-generation sphalerite. The data for 10 samples fall between 5.410(8) and 5.412(3) Å, but the data for the other four samples fall between 5.418(7) and 5.421(3) Å. There is no correlation with color, sample location or difference in age. The cause of these large variations, which are far greater than those expected on the basis (Barton & Skinner 1967) of the small chemical variations (Table 1) are not known. X-ray powder diffraction of smear mounts reveals only reflections typical of sphalerite, but precession photographs of anisotropic


FIG. 3. Photomicrograph in transmitted plane-polarized light of a Gordonsville specimen illustrating the two generations of sphalerite, an organic-inclusion-rich first phase and an inclusion-free second phase. Width of field is 3 cm.

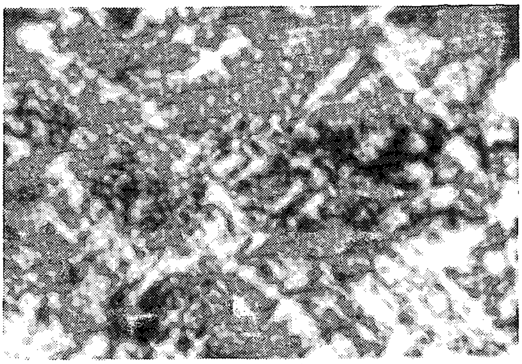
FIG. 4. Transmitted-light photomicrograph taken with crossed nicols to illustrate the "gridiron"-type anisotropy. Width of field is 1 mm.

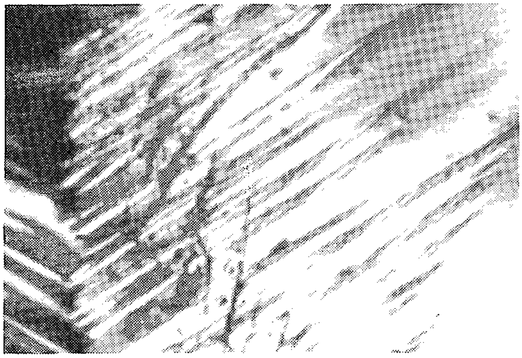
FIG. 5. Transmitted-light photomicrograph taken with crossed nicols to illustrate *en échelon* twinning in Elmwood–Gordonsville sphalerite. The irregular black specks are hydrocarbon-containing inclusions. Width of field is 1 mm.

TABLE 1. REPRESENTATIVE COMPOSITIONS OF SPHALERITE FROM THE ELMWOOD-GORDONSVILLE DEPOSITS

			(weight %)		
Sample	Zn	Fe	Cd	S	Total
First generation	66.14	0.47	0.47	31.87	98.95
"	66.46	0.51	0.56	32.12	99.65
"	66.43	0.54	0.65	32.13	99.75
Second generation	67.08	0.17	0.13	32.23	99.61
"	66.86	0.25	0.26	32.45	99.72
"	66.72	0.49	0.45	32.62	100.28
First generation (av. 45 analyses)	-	0.49	0.57	-	-
Second generation (av. 55 analyses)	-	0.36	0.30	-	-
High-birefringence area (Fig. 7)	-	0.31	0.32	-	-
Surrounding area	-	0.22	0.20	-	-

Compositional data determined by electron-microprobe analysis. Synthetic sulfides were used as standards.

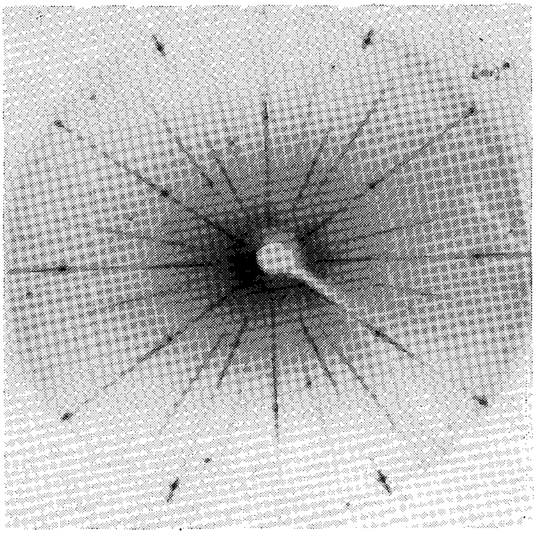

FIG. 6. Zero-level [110]-axis precession photograph of sample G-4: Cu$K\alpha$, $\mu = 30°$, four-day exposure. Note streaking parallel to [111]*, as well as reflections due to twinning.

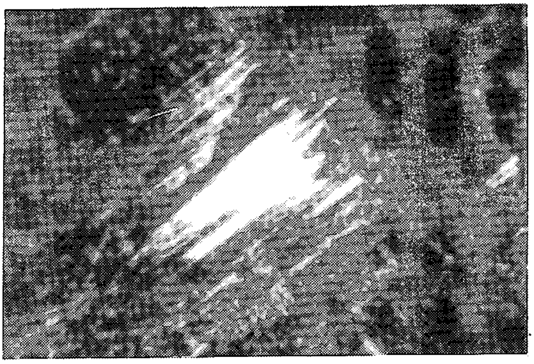

FIG. 7. Transmitted-light photomicrograph of Elmwood–Gordonsville sphalerite, taken with crossed nicols, illustrating a zone of strong anisotropy that is also richer in iron and cadmium than the surrounding area (see Table 1). Width of field is 2.5 mm.

sphalerite display diffraction streaks parallel to one of the four symmetry-equivalent <111> directions (Fig. 6). These streaks thus represent small domains of stacking disorder along that direction. Reflections associated with a twin axis parallel to that direction are also present.

Electron-microprobe analyses (Table 1) indicate that the first-generation sphalerite averages 0.49 wt.% Fe and 0.57 % Cd; the second-generation sphalerite averages 0.36 % Fe and 0.30 % Cd (Craig *et al.* 1983). A traverse beginning in an area of low birefringence, across an area of higher birefringence (Fig. 7), and then back to an area of low birefringence revealed that the Fe and Cd contents were approximately 50% higher in the area of greater birefringence (Table 1).

Reflectances for first- and second-generation sphalerite were measured, respectively, as 18.0% and 16.3% at 460 nm, 15.7% and 16.0% at 546 nm, and 14.7% and 19.7% at 650 nm. These values are consistent with those obtained for other samples of sphalerite with approximately 0.5 wt.% iron (Vaughan & Craig 1978).

Homogenization- and freezing-temperature studies were conducted on primary fluid-inclusions in first-generation sphalerite and fluorite. Uncorrected temperatures of homogenization measured on inclusions range from 125° to 132°C in the sphalerite and from 108° to 116°C in the fluorite. Freezing-point temperatures of inclusions in sphalerite and fluorite range from −19.6° to −20.1°C and from −13.9° to −14.8°C, respectively. These temperatures indicate salinites of approximately 22.2 and 18.4 wt.% (NaCl equivalent) for the fluid inclusions in the sphalerite and fluorite, respectively. These homogenization and freezing temperatures are similar to those reported by Roedder (1976). Upon heating of solidly frozen inclusions, the initial melting was first observed at about −33°C for the sphalerite and about −30°C for the fluorite; this suggests that the fluids contain additional salts such as $CaCl_2$ or $MgCl_2$. Unfortunately, the appropriate pressure-correction to apply to these fluid inclusions is difficult to estimate because the age of the mineralization is not known.

DISCUSSION

The Elmwood–Gordonsville deposits are typical Mississippi-Valley-type ores. The fluid-inclusion data for the sphalerite and fluorite, though limited, are consistent with an ore-forming fluid that exhibited a slight decrease in salinity and temperature with time during ore deposition. Electron-microprobe analysis indicates that the compositions of the Elmwood–Gordonsville sphalerite range from 0.14 to 0.60 wt.% Fe (average 0.36 %) and from 0.09 to 0.72 wt.% Cd (average 0.36 %). X-ray powder diffraction reveals that most of the unit-cell parameters are consistent with those expected of sphalerite with approximately 0.5 wt.% Fe and 0.5 wt.% Cd (Barton & Skinner 1967), but that some values are unexpectedly large.

X-ray-precession photographs (Fig. 6) display diffraction streaks along reciprocal lattice rows with $h+k \neq 3n$ (equivalent hexagonal indices), indicating stacking disorder in the sphalerite (Fleet 1977b). The stacking faults and twinning create domains of nonisometric symmetry that are optically anisotropic (Fleet 1977a,b). Using the linear relationship between birefringence δ and volume % hexagonal close-packed layers σ observed by Nelkowski & Pfützen-Reuter (1971) and Fleet (1977a), σ averages 5% and ranges from 0 up to 38% in small domains in the samples studied.

The zinc sulfide mineralization of the Elmwood–Gordonsville deposits fills collapse breccias and open cavities. Sphalerite is the only zinc sulfide found in the deposits, and ore textures such as growth banding paralleling sphalerite-type crystal faces suggest that it was primary; accordingly, transformation from wurtzite seems to be an unlikely explanation for the anisotropy. Furthermore, M.E. Fleet (pers. comm. 1984) has pointed out that sphalerite transformed from wurtzite would have twin orientations present in equal proportions; the twin orientations in the samples examined are unequal. The structural setting, the undistorted nature of the crystals, and the open nature of the mineralized cavities apparently preclude structural deformation as the cause of the anisotropy. Uncorrected temperatures of homogenization above 135°C were not observed in primary fluid-inclusions; thus, the thermal-stress mechanisms described by Akizuki (1970, 1981) seem to be an unlikely explanation for the anisotropy of sphalerite, because they are reported to occur at temperatures in excess of 900°C.

Geilikman (1982) suggested that cadmium atoms replacing zinc atoms in zinc sulfide stabilize a hexagonal (wurtzite) structure because pure cadmium sulfide (greenockite) has hexagonal symmetry at the temperatures in question. Because the electron-microprobe data demonstrate that Cd and Fe are higher in areas of higher birefringence in the sphalerite, the hexagonal symmetry of small domains that impart the anisotropic character to the sphalerite is probably stabilized by the cadmium and iron replacing zinc in the structure. Furthermore, the birefringent textures extend across the contacts of first- and second-generation sphalerite apparently undisturbed; thus the anisotropy appears to result from growth defects causing stacking disorder and twinning that formed contemporaneously with the deposition of the sphalerite.

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