

## ARGENTITE AND ACANTHITE

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Silver sulphide is found in nature in crystals which have been referred to the isometric system (argentite) and others which have been referred to the orthorhombic system (acanthite). The existence of acanthite as anything more than deformed argentite has been called in question by Krenner.<sup>1</sup> Argentite is commonly regarded as isomorphous with galena.<sup>2</sup> Recently Ramsdell<sup>3</sup> has shown that argentite and acanthite give identical X-ray patterns which are not isometric and he has concluded that they "do not represent distinct mineral species"; he has also argued that argentite can not be isomorphous with galena since it is not isometric. It is the object of this note to present additional evidence bearing on these points.

It is known<sup>4</sup> from studies of the thermal properties and electric conductivity of silver sulphide that the substance undergoes a reversible inversion<sup>5</sup> at about 180°C; this inversion takes place very easily and promptly on cooling as well as on heating. It is evident from the work of Ramsdell that the low temperature form of the substance is not isometric, and it is probable from crystallographic study of acanthite that the low temperature form is orthorhombic. The chief problem, then, is to determine the symmetry of the high temperature form of silver sulphide. The writers undertook to accomplish this task by means of X-ray patterns of the substance. Since silver sulphide changes in symmetry at about 180°C on both heating and cooling, no X-ray pattern obtained at ordinary temperature would give any information regarding the symmetry of the high temperature form, but a pattern obtained at any<sup>6</sup> temperature above 180°C would solve the problem, if it could be interpreted.

In order to obtain an X-ray pattern of silver sulphide at a temperature above 180°C the tiny glass tube containing the

<sup>1</sup> Dana: System of Mineralogy, p. 58, 1892.

<sup>2</sup> See the textbooks of Dana, Bayley, Rogers, Kraus and Hunt, etc.

<sup>3</sup> *Am. Mineral.*, X, 1925, p. 281.

<sup>4</sup> *Zeit. anorg. Chem.*, CXVII, p. 17, 1921.

<sup>5</sup> Urazov (*Min. Abst.* II, 1923, p. 154) reached the conclusion from thermal studies that silver sulphide is even tetramorphous.

<sup>6</sup> Assuming no inversion at a temperature above 180°C.

powdered substance was mounted between two strips of lead or lead glass which are opaque to X-rays. In a slot along the edge of each strip and close to the powdered mineral was placed a nichrome wire<sup>7</sup> for heating purposes. The tube was held in place and thermal insulation between the tube and the wire reduced by means of bakelite cement. A thermocouple was mounted at the end of the glass between the heating wires. The wires of the thermocouple were not exposed to the X-rays; and the heating wires were screened from these rays by the opaque lead or lead glass.

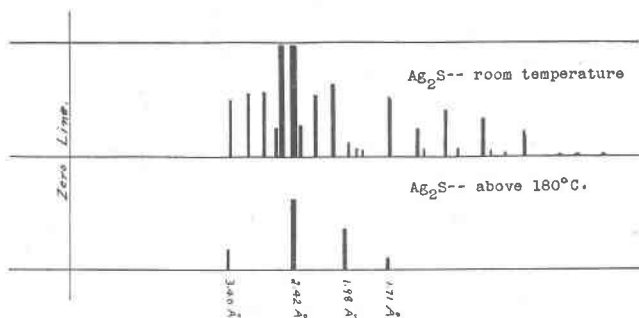


FIG. 1

Diagrams of X-ray patterns from powders of  $\text{Ag}_2\text{S}$ . Upper part taken below  $180^\circ\text{C}$  and lower part above  $180^\circ\text{C}$ . Width of lines proportional to width in photographs and length of lines proportional to intensity.

The X-ray patterns of silver sulphide at room temperature and also at  $200\text{--}250^\circ\text{C}$  are shown side by side in Fig. 1. The pattern at room temperature from argentite (and also from artificial silver sulphide) is complicated and, as reported by Ramsdell, is identical with that produced by acanthite. The X-ray pattern of silver sulphide above  $180^\circ\text{C}$  is simple and quite different from that produced at room temperature. This simple pattern, which consists of only four distinguishable lines, fits the chart of the pattern of crystals whose atoms are arranged in a body-centered cubic lattice.<sup>8</sup> On this basis the calculated specific gravity of the substance is 7.2, which checks well with the specific gravity of the argentite (7.2–7.36) as given by Dana. The four lines of the pattern also fit the chart of the patterns of crystals with simple cubic lattices, but the calculated specific gravity in this case is 10.4. The atomic weight of sulphur is small compared with that of

<sup>7</sup> When using lead as a screen the wire was insulated by means of mica.

<sup>8</sup> W. P. Davey: *Gen. Elec. Rev.*, XXV, p. 565, 1922.

silver so that reflections from planes of sulphur atoms may be too faint to be distinguishable. The stable form of silver sulphide above 180°C is therefore isometric and the lattice producing a visible X-ray pattern is body-centered; it seems probable that this lattice consists of silver atoms; the arrangement of the sulphur atoms has not been determined. The line on the pattern at 3.40 Ångstroms is the first order reflection from the (110) planes; the line at 2.42 Ångstroms is the second order reflection from the (100) planes; the line at 1.98 Ångstroms is the first order reflection from the (112) planes; and the line at 1.71 Ångstroms is the second order reflection from the (110) planes. The side of the elementary cube is 4.84 Ångstroms.

From these facts the following conclusions can be drawn:

1. Above 180°C the stable form of silver sulphide is isometric with a body-centered space lattice.

2. All silver sulphide at ordinary temperature—no matter whether it is natural argentite or natural acanthite or the artificial substance—has the same space lattice as acanthite and is probably orthorhombic.

3. Externally isometric natural crystals of silver sulphide were formed at temperatures<sup>9</sup> above 180°C, and at ordinary temperature are acanthite paramorphs after argentite.

4. Argentite and acanthite are both true and independent mineral species, though argentite exists as such only at temperatures above 180°C.

5. Above 180°C argentite and galena may be miscible to some extent in the crystal state since they are both isometric, but the miscibility is probably very limited not only because of the difference in the formulas, but also because argentite has a body-centered lattice while galena has the NaCl type of lattice, and finally because the length of the side of the unit cube of argentite (4.84 Ångstroms) differs decidedly from the same measure for galena<sup>10</sup> (5.93 Ångstroms). Therefore, according to present evidence argentite and galena should not be considered as isomorphous.

The authors take pleasure in acknowledging the helpful cooperation of Miss Emilie Hahn in the foregoing study of argentite and acanthite, which was made under the supervision of Professor A. N. Winchell.

<sup>9</sup> Disregarding the influence of pressure and impurities upon the inversion temperature.

<sup>10</sup> L. S. Ramsdell: *op. cit.* p. 283.