

# Crystal structure refinement of miargyrite, $\text{AgSbS}_2$

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## Abstract

Miargyrite is the low-temperature monoclinic derivative of a high-temperature cubic galena/halite structure. The essential features of its crystal structure (Knowles, 1959) were confirmed, but the details of the bonding changed [new space group  $C121$ ;  $a$  12.824(1),  $b$  4.4060(3),  $c$  13.193(1) Å,  $\beta$  98.567(6)°]. The octahedral connectivity of galena/halite is severely distorted: Ag(1), 2S each at 2.53, 2.66 & 3.39 Å; Ag(2), 2 each at 2.54, 2.62 and 3.44; Ag(3), 2.38, 2.40, 3.05, 3.05, 3.53, 3.58; Sb(1), 2.45, 2.50, 2.51, 3.22, 3.28, 3.41; Sb(2), 2.45, 2.50, 2.51, 3.22, 3.28, 3.41. The short distances define the following coordinations: very distorted tetrahedral Ag(1) and (2); near-linear Ag(3) at 178.9(2)°; trigonal-pyramidal Sb(1) and (2) at 92.0, 93.6 and 96.8°. The ten shortest S–S distances range from 3.61 to 3.77 Å.

KEYWORDS: miargyrite, crystal structure,  $\text{AgSbS}_2$

## Introduction

MANY heavy chemical elements have multiple valence states and complex bonding arrangements in crystal structures that are poorly understood. Most can be toxic to biological organisms. All have complex geochemical behaviours that are directly or indirectly important for human welfare.

Miargyrite,  $\text{AgSbS}_2$ , was chosen for detailed study because it contains medium-heavy elements suitable for pioneering new synchrotron X-ray techniques in diffraction and absorption spectroscopy (reviews: Smith, 1995; Smith and Rivers, 1995). Silver has many industrial applications, and antimony is toxic to biological organisms at high concentration. Furthermore, the complex phase equilibria, solid solution with Se, and semiconducting electronic properties have been investigated by solid-state physicists (Geller and Wernick, 1959; Kelleher *et al.*, 1996).

The room-temperature structure of miargyrite is a highly distorted derivative of the high-temperature disordered halite/galena structure (Knowles, 1959). We refined the room-temperature structure, and changed the space group from  $C1c1$  to  $C121$ .

## Experimental

Knowles (1959) ground a near-spherical crystal with mean diameter 0.11 mm, and collected data with a hand-operated diffractometer. With modern higher-efficiency counters, a smaller crystal could be used in order to reduce the absorption correction. Furthermore, computer-controlled automation allowed collection of many more diffractions. A fragment from the same mineral specimen, Mineralogical Museum, University of Toronto, #R569, was chopped with a razor blade to  $0.15 \times 0.13 \times 0.11$  mm, and mounted on an automated Picker four-circle diffractometer with the  $b$  axis offset a few degrees from the  $\phi$  axis. Data were collected at 20°C using an 8 kW rotating anode source with Mo radiation.

Collection of 10,361 diffractions used the  $\theta$ – $2\theta$  step-scan technique, 0.02°/step, counting for 0.2 sec/step, scan width 3° with a  $2\theta$  range of 3–80°. Merging yielded 4605 diffractions ( $R_{\text{int}} = 0.021$ ), all of which were used in the refinement. Three standard diffractions stayed constant within 1.4 %, and the data collection range was  $h \pm 23$ ,  $k \pm 7$ ,  $l \pm 23$ . The absorption correction used a local program based

TABLE 1. Atomic coordinates and displacement parameters

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub>
Ag(1)	0	0	0	0.0354(4)
Ag(2)	0	0.9409(3)	0.5	0.0373(4)
Ag(3)	0.00047(7)	0.4700(8)	0.24993(7)	0.0448(2)
Sb(1)	0.25543(4)	0.9306(7)	0.37660(3)	0.0200(2)
Sb(2)	0.74466(4)	0.9998(7)	0.12335(3)	0.0193(2)
S(1)	0.14338(13)	0.3140(10)	0.44958(11)	0.0189(4)
S(2)	0.85659(13)	0.6144(10)	0.05053(11)	0.0205(5)
S(3)	0.11168(13)	0.1438(11)	0.16765(13)	0.0215(5)
S(4)	0.88833(14)	0.7853(11)	0.33252(13)	0.0241(5)

Atom	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
Ag(1)	0.0258(3)	0.0453(11)	0.0331(4)	0	-0.0021(3)	0
Ag(2)	0.0249(3)	0.0474(10)	0.0382(4)	0	0.0008(3)	0
Ag(3)	0.0347(2)	0.0615(3)	0.0408(2)	-0.0113(2)	0.0143(2)	0.0150(2)
Sb(1)	0.0236(2)	0.0212(3)	0.0153(2)	-0.0009(2)	0.0037(1)	-0.0010(2)
Sb(2)	0.0232(2)	0.0196(3)	0.0152(2)	-0.0001(2)	0.0035(1)	0.0002(2)
S(1)	0.0184(5)	0.0215(13)	0.0169(5)	0.0004(10)	0.0029(4)	-0.0019(10)
S(2)	0.0184(5)	0.0266(12)	0.0164(5)	-0.0008(9)	0.0019(4)	0.0022(10)
S(3)	0.0213(6)	0.0227(13)	0.0218(6)	0.0004(11)	0.0075(5)	-0.0005(10)
S(4)	0.0219(7)	0.0298(14)	0.0218(6)	0.0035(11)	0.0076(5)	0.0032(10)

TABLE 2. Interatomic distances (Å) and angles (°)

Ag(1)—S(3), twice	2.530(2)	S(1)—S(1), twice	3.608(3)
Ag(1)—S(2), twice	2.660(3)	S(2)—S(2), twice	3.608(3)
Ag(1)—S(2), twice	3.394(4)	S(1)—S(4)	3.618(3)
Ag(2)—S(4), twice	2.542(2)	S(2)—S(3)	3.619(3)
Ag(2)—S(1), twice	2.625(3)	S(1)—S(4)	3.703(2)
Ag(2)—S(1), twice	3.438(4)	S(2)—S(3)	3.703(2)
Ag(3)—S(4)	2.378(3)	S(1)—S(3)	3.757(2)
Ag(3)—S(3)	2.396(3)	S(2)—S(4)	3.758(2)
Ag(3)—S(2)	3.047(2)	S(1)—S(4)	3.769(3)
Ag(3)—S(1)	3.055(2)	S(2)—S(3)	3.774(3)
Ag(3)—S(3)	3.534(4)	S(3)—Ag(1)—S(3)	151.0(2)
Ag(3)—S(4)	3.581(4)	S(3)—Ag(1)—S(2), twice	105.3(1)
Sb(1)—S(4)	2.446(3)	S(3)—Ag(1)—S(2), twice	93.2(1)
Sb(1)—S(1)	2.502(3)	S(2)—Ag(1)—S(2)	100.6(2)
Sb(1)—S(1)	2.514(2)	S(4)—Ag(2)—S(4)	148.7(2)
Sb(1)—S(3)	3.220(2)	S(4)—Ag(2)—S(1), twice	93.7(1)
Sb(1)—S(1)	3.284(3)	S(4)—Ag(2)—S(1), twice	105.9(8)
Sb(1)—S(4)	3.409(3)	S(1)—Ag(2)—S(1)	102.5(2)
Sb(2)—S(3)	2.451(3)	S(4)—Ag(3)—S(3)	178.9(2)
Sb(2)—S(2)	2.505(3)	S(4)—Sb(1)—S(1)	96.9(1)
Sb(2)—S(2)	2.513(2)	S(4)—Sb(1)—S(1)	93.7(1)
Sb(2)—S(4)	3.223(2)	S(1)—Sb(1)—S(1)	92.0(1)
Sb(2)—S(2)	3.276(3)	S(3)—Sb(2)—S(2)	96.7(1)
Sb(2)—S(3)	3.406(3)	S(3)—Sb(2)—S(2)	93.6(1)
		S(3)—Sb(2)—S(2)	91.9(1)

on the analytical method for an ideal rhombic prism, with 0.31 and 0.19 as the maximum and minimum absorption corrections ( $\mu = 13.48 \text{ mm}^{-1}$ ).

The choice of space group is not trivial. The systematic absences almost fit  $C12/c1$ , but we found 60 diffractions that violate the  $1c1$  glide. We found that  $C121$  provided a satisfactory refinement. Knowles used two Ag atoms in  $Cc$ . In  $C121$ , the Ag(1) from Knowles was split into Ag(1) and Ag(2). The origin of the unit cell is not fixed by the space group symmetry, and was deliberately placed at Ag(1). The Ag(2) position of Knowles was renumbered Ag(3). The Sb and S positions carry

over unchanged. Using SHELXL93 (Sheldrick, 1993), least-squares refinement against  $F^2$  was performed using neutral scattering factors, first with isotropic and then anisotropic thermal parameters.

In the final model, 74 refined parameters yielded weighted  $R(wR^2)$  of 0.117.  $R(F)$  is 0.049.  $S = 1.17$ , and maximum and minimum heights on the final difference Fourier map  $+4.1$  and  $-3.2 \text{ e}\text{\AA}^{-3}$ , located near Sb. Local data reduction and cell refinement programs were used. Final atomic coordinates and displacement parameters are given in Table 1, and selected bond distances and angles in Table 2.

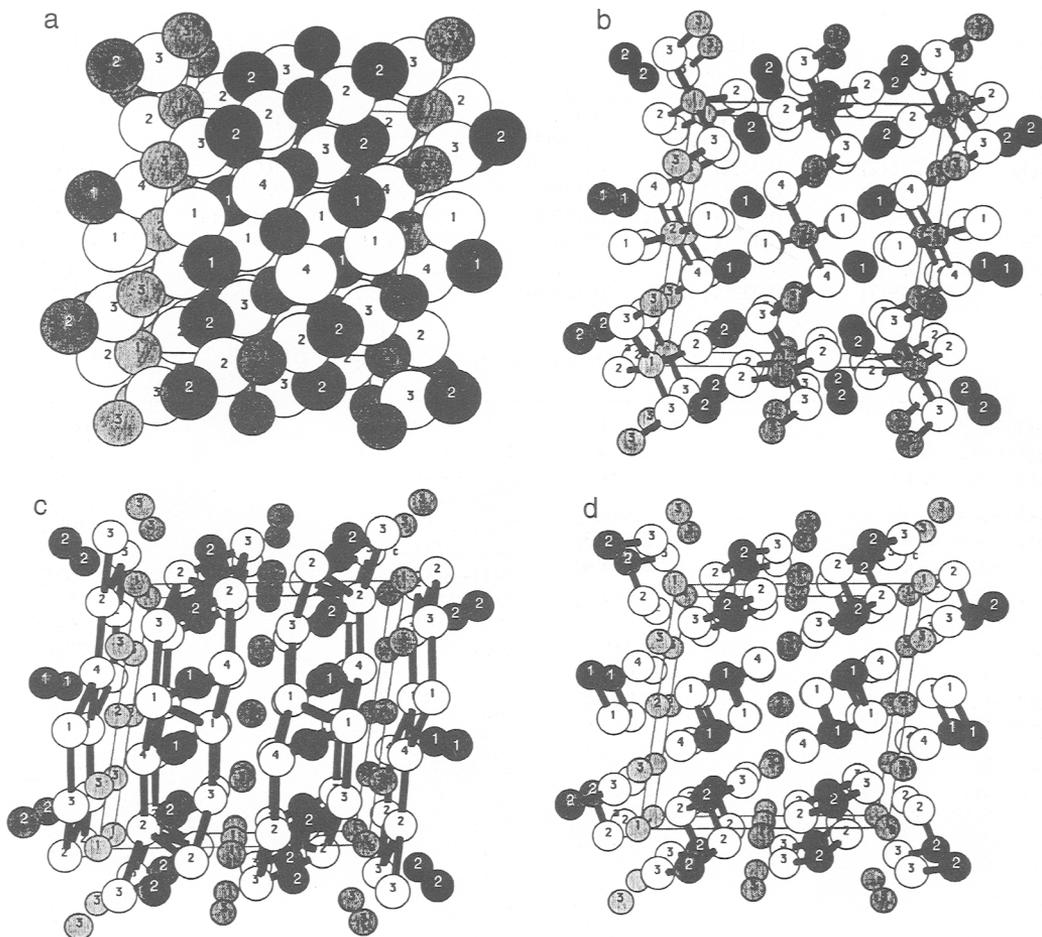


FIG. 1. Atomic packing of miargyrite projected down the *b* axis with two unit cells in disappearing perspective. The *a* axis is near-horizontal, and *c* is near-vertical. S, open; Ag, light stipple; Sb, heavy (and white numerals). Numbers show atom type. Upper left (a) packing diagram using conventional atomic radii. Upper right (b) bonding diagram for Ag. Lower right (c) bonding diagram for Sb. Lower left (d) ten shortest S-S connections. Drawn with Crystal Structure Design AS, Blindern POB 24, Oslo, Norway.

### Discussion

The essential connectivity of the structure is unchanged (Knowles, 1959, Fig. 1) but the interatomic distances have changed and become more accurate (Figs. 1 and 2).

The packing diagram (Fig. 1*a*) shows the relation to the galena/halite structure, and the sub-diagrams (Fig. 1*b,c*) show how each metal atom is closely linked to only some of the six octahedral neighbours in galena/halite. The Ag atoms form a corrugated planar net in (100). In contrast, the Sb atoms form double-rods parallel to *b*.

Silver (1) and (2) have essentially the same coordination with distances that differ only by a few sigma. Fig. 2*a* shows Ag(1) with its four bonded S in a distorted tetrahedron viewed down *a*, plus the two non-bonded S from the galena structure type. Fig. 2*b* shows only the four bonded S viewed down *b*. Fig. 2*c* shows the four bonded S and two unbonded S of Ag(2). Specifically for Ag (1) and (2) there are two near S at 2.53/2.54 Å, two more distant at 2.66/2.62, and two very distant at 3.39/3.44 Å. Silver (3) has two near S at 2.38 and 2.40 Å (Fig. 2*d*), and four

distant ones at 3.05, 3.06, 3.53 and 3.58 Å. The two near S are nearly collinear at 178.9°. Antimony (1) and (2) have identical coordination within the one-sigma level (Fig. 2*e,f*): three near S at the vertices of a trigonal pyramid at 2.45, 2.50 and 2.51 Å and three distant ones at 3.22, 3.28 and 3.41 Å.

The ten shortest S–S distances (3.61 to 3.77 Å) generate a double-layer net (Fig. 1*d*) that lies between the bonding connections of the Ag and Sb atoms.

To conclude, the present structure determination demonstrates the current level of accuracy obtainable with a laboratory X-ray source for a dense material. The next stage of miargyrite refinement will profit from synchrotron X-ray techniques using ~100 keV photons to get lower absorption error and extinction. Tuning through the K edges of Ag and Sb with a polarized beam should provide information on the angular distribution of the bonding electrons. Study of the phase transition(s) to the disordered high-temperature phase should provide a test of dynamic models. Reduction of the temperature towards absolute zero should test whether further phase changes occur.

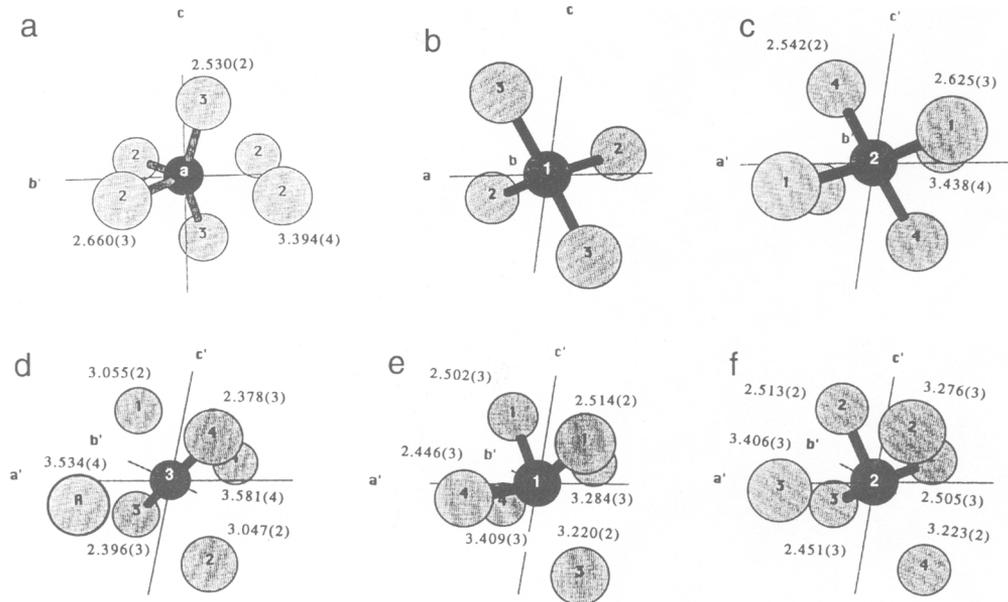


FIG. 2. Nearest S atoms to Ag and S. Distance in Å with one-sigma error. Upper left (a) Ag(1) viewed down *a*. The S atoms occur as three symmetry pairs, two bonded and one unbonded. Upper center (b) Ag(1) viewed with *b* tilted northwest; unbonded S omitted. Upper right (c) Ag(2) showing one unbonded and two bonded pairs of S. Lower left (d) Ag(3) with two bonded and four unbonded S. Lower center (e) Sb(1) with three bonded and three unbonded S. Lower right (f) Sb(2) with matching coordination to Sb(1), except for change of orientation.

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### References

- Geller, S. and Wernick, J.H. (1959) Ternary semi-conducting compounds with sodium chloride-like structure:  $\text{AgSbSe}_2$ ,  $\text{AgSbTe}_2$ ,  $\text{AgBiS}_2$ ,  $\text{AgBiSe}_2$ . *Acta Crystallogr.*, **12**, 46–54.
- Kelleher, I., Redfern, S.A.T. and Pattrick, R.A.D. (1996) Cadmium substitution in miargyrite ( $\text{AgSbS}_2$ ) and related phases: an experimental reconnaissance. *Mineral. Mag.*, **60**, 393–401.
- Knowles, C.R. (1959) A redetermination of the structure of miargyrite,  $\text{AgSbS}_2$ . *Acta Crystallogr.*, **17**, 847–51.
- Sheldrick, G.M. (1993) SHELXL93. *Program for the Refinement of Crystal Structures*. Univ. Gottingen, Deutschland.
- Smith, J.V. (1995) Synchrotron X-ray sources: Instrumental characteristics. New applications in microanalysis, tomography, absorption spectroscopy and diffraction. *Analyst*, **120**, 1231–45.
- Smith, J.V. and Rivers, M.L. (1995) Chapter 5 Synchrotron X-ray microanalysis. In *Microprobe Techniques in the Earth Sciences*, (P.J. Potts, J.F.W. Bowles, S.J.B. Reed and M.R. Cave, eds.) Chapman and Hall, p. 163–233.

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