

## The crystal structure of covellite CuS under high pressure up to 33 *kbar*

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### *High pressure / Covellite / CuS*

**Abstract.** The crystal structure of covellite has been studied under pressure up to 33 *kbar* based on single-crystal diffraction intensities collected with a four-circle diffractometer. The contraction of the unit cell takes place in such a way that the axial ratio  $c/a$  is kept nearly constant, the cell volume at 1 *bar* being reduced by about 5% at 33 *kbar*. With the contraction of the Cu–S bonds the sulfur-sulfur bond of the S<sub>2</sub> group shows a trend of lengthening in a way similar to the relation between S–S and M–S bonds in the compounds MS<sub>2</sub> (M = Cu, Ni, Co, Fe) having the pyrite structure type.

### Introduction

Covellite CuS is a *p*-type metal (Shuey, 1975) and has been known as a representative superconducting compound (London, 1950). The crystal structure, which was analyzed by Oftedal (1932) and confirmed by Berry (1954), has been refined by Bernardini and Catani (1968), Kalbskopf, Pertlik and Zemann (1975), Evans and Konnert (1976), and Ohmasa, Suzuki and Takéuchi (1977). The structure is built up of a layer consisting of CuS<sub>3</sub> triangles and CuS<sub>4</sub> tetrahedra, the layer being joined together with its adjacents by sulfur-sulfur bonds to attain the continuity of the structure. The structure of covellite is thus characteristic of having S<sub>2</sub> groups. The S–S bond length of the group has been reported to be 2.071(4) Å (Evans and Konnert, 1976) which is close to 2.086(7) Å obtained by Ohmasa et al. (1977) and to 2.09 Å by Berry (1954).

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These values are significantly larger than the S–S bond length 2.0300(6) Å for the S<sub>2</sub> groups of CuS<sub>2</sub> (King and Prewitt, 1979) and smaller than 2.259(5) Å for those of pyrite FeS<sub>2</sub> (Finklea, Cathey and Amma, 1976). It is notable that the S–S lengths in the compounds MS<sub>2</sub>, having the pyrite structure type, vary depending upon the distance between M and S (Elliott, 1960). It is then of particular interest to observe the effect of compression of the Cu–S bonds in the covellite structure on its S–S bond. The structural study of covellite under high pressure was therefore undertaken with the result as reported in the present paper. A brief account has appeared earlier (Takéuchi, Kudoh and Sato, 1979).

### Experimental

Crystals used for the present study were from Kosaka mine, Akita Prefecture, Japan, and provided by the University Museum, University of Tokyo (sample number: UTUMMI-00313); those of the same sample number had been used by Ohmasa et al. (1977) for structure refinement. Out of a large platy crystal, about 5 mm wide, we prepared three crystal pieces, which we denoted # 1, # 2, and # 3, approximately having the dimensions 0.15 × 0.15 × 0.02 mm.

To apply high hydrostatic pressure, we used a diamond anvil cell which was essentially of the Merrill-Bassett type (Merrill and Bassett, 1974) but with a slight modification. It was designed (Takéuchi, 1980) in such a way that one of the pair of the Be disks was allowed a hemispherical mount in the metal frame. By applying a small amount of molybdenum paste between the contact surfaces of the Be disk and the frame, we can readily keep the parallel position of the pair of the diamond anvil crystals during the application of pressure. For gasket, we used an Inconel X750 plate of 0.25 mm thick; the diameter of the hole opened in the gasket to mount the crystal specimen was 0.30 mm. As fluid-pressure medium, cedar oil or a 1:1 mixture of pentane and isopentane were used.

In the gasket hole, a fragment of NaCl or CsCl single crystal was put together with the covellite specimen to evaluate the pressure in terms of the change of cell dimensions of NaCl or CsCl, using Decker's equation of state (Decker, 1971); the size of these reference crystals were nearly the same as that of the covellite specimens. The pressures applied are listed in Table 1 together with the specimens, fluid media and reference crystals used.

The unit-cell dimensions were obtained with a least-squares procedure applied to  $\sin 2\theta$  values of 11 ~ 15 reflections measured on a Syntex P2<sub>1</sub> four-circle single-crystal diffractometer, using graphite monochromated MoK<sub>α</sub> radiation ( $\lambda = 0.71068$  Å). They are summarized in Table 2. The unit cell contains 6 × CuS. No change of space group symmetry (*P*6<sub>3</sub>/*mmc*) was observed in the pressure range covered.

**Table 1.** Intensity-study data

Pressure (kbar)	6	12	18	21	29	33
Specimen number	# 3	# 3	# 2	# 1	# 1	# 3
Pressure medium	Cedar oil			Pentane + isopentane		
referenc crystal	NaCl			CsCl		
No. of independent reflections						
measured	—	70	49	45	—	32
used	—	27	31	32	—	21
<i>R</i> %	—	8.4	8.7	5.0	—	11.4
<i>wR</i> %	—	5.3	4.1	2.2	—	6.0

**Table 2.** Unitcell parameters of covellite under pressure up to 33 *kbar* (those for 1 *bar* are after Ohmasa et al. 1976)

Pres- sure	1 bar	6 kbar	12 kbar	18 kbar	21 kbar	29 kbar	33 kbar
<i>a</i> (Å)	3.796(1)	3.773(3)	3.768(3)	3.760(1)	3.757(1)	3.729(3)	3.729(2)
<i>c</i> (Å)	16.382(5)	16.30(8)	16.27(6)	16.20(4)	16.19(2)	16.10(8)	16.11(6)
<i>V</i> (Å <sup>3</sup> )	204.4(1)	200.9(9)	200.0(6)	198.3(4)	198.0(2)	193.9(9)	194.0(6)
<i>c/a</i>	4.316(2)	4.32(2)	4.32(2)	4.31(1)	4.31(1)	4.32(2)	4.32(2)

The diffraction intensities were collected at 12 *kbar*, 18 *kbar*, 21 *kbar* and 33 *kbar*. In the first case, the psi-scan technique as developed by Denner, Schulz and D'Amour (1978) was employed to measure the intensities. While in the remaining cases, the fixed-phi technique (Finger and King, 1978) was used. The number of the diffraction intensities, including symmetry equivalents, thus measured was 1160 at 12 *kbar* and 185 ~ 209 at the remaining pressures. The reflections from the reference crystal or the paired diamond anvil crystals were rejected according to the procedure provided by Denner et al. (1978). After correction for Lorentz and polarization factors and for absorption, the intensities were reduced to structure factors. The number of independent structure factors obtained in each case is given in Table 1.

### Structure refinement

Among structure factors, those greater than  $2\sigma|F_o|$  were used for structure refinements (Table 1) which were carried out with the least-squares program LINUS (Coppens and Hamilton, 1970); a weighting scheme of the form  $1/(\sigma|F_o|)^2$  was used. The atomic parameters reported by Ohmasa et al.

**Table 3.** Atomic coordinates and isotropic temperature factors of covellite under pressure up to 33 *kbar* (those at 1 *bar* are after Ohmasa et al. 1976)

Pressure		1 bar	12 kbar	18 kbar	21 kbar	33 kbar
Cu(1)	<i>x</i>	1/3	1/3	1/3	1/3	1/3
	<i>y</i>	2/3	2/3	2/3	2/3	2/3
	<i>z</i>	3/4	3/4	3/4	3/4	3/4
	<i>B</i> (Å <sup>2</sup> )	2.90	5.9(6)	5.4(6)	2.9(2)	5(1)
Cu(2)	<i>x</i>	1/3	1/3	1/3	1/3	1/3
	<i>y</i>	2/3	2/3	2/3	2/3	2/3
	<i>z</i>	0.10724(9)	0.1107(13)	0.1111(5)	0.1197(4)	0.123(2)
	<i>B</i> (Å <sup>2</sup> )	1.20	0.9(2)	0.8(2)	0.32(6)	0.4(4)
S(1)	<i>x</i>	1/3	1/3	1/3	1/3	1/3
	<i>y</i>	2/3	2/3	2/3	2/3	2/3
	<i>z</i>	1/4	1/4	1/4	1/4	1/4
	<i>B</i> (Å <sup>2</sup> )	1.70	6(1)	1.4(3)	0.7(2)	1(1)
S(2)	<i>x</i>	0	0	0	0	0
	<i>y</i>	0	0	0	0	0
	<i>z</i>	0.0637(2)	0.066(3)	0.069(1)	0.069(1)	0.076(4)
	<i>B</i> (Å <sup>2</sup> )	0.84	1.4(5)	2.0(2)	2.8(2)	1(1)

(1977) served for providing initial atomic coordinates for the refinements. Although only *z* for Cu(2) and *z* for S(2) are the variable positional parameters, we encountered with the following problem in refining the structure.

The problem laid on the fact that the (001) plane of the specimen was parallel to the tables of the diamond anvil crystals, thus giving a restriction upon the range of index *l* to be covered. Although we were able to cover up to *l* = 7 at pressure 21 *kbar*, and *l* = 6 at other pressures applied, we observed a relatively large correlation between the two *z* parameters; the correlation coefficients ranged from 0.36 in the case of 18 *kbar* to 0.49 in the case of 21 *kbar*. Nevertheless, the refinement in each case smoothly converged to give the final value of *R* as listed in Table 1. The final shifts of the *z* parameters were smaller than one tenth of the estimated errors. Because of the above-mentioned correlation, the figures of the estimated errors would perhaps be of less reality. The result as a whole, however, is thought to reflect the general trend of the effect of pressure on the structure. The atomic form factors for neutral Cu and S were provided by the *International Tables for X-ray Crystallography* (1962). In Table 3 we give the final atomic parameters.

## Result and discussion

As will be observed in Figure 1, which shows the variation of cell dimensions relative to those at 1 *bar*, the compressibilities of *a* and *c*, are nearly the

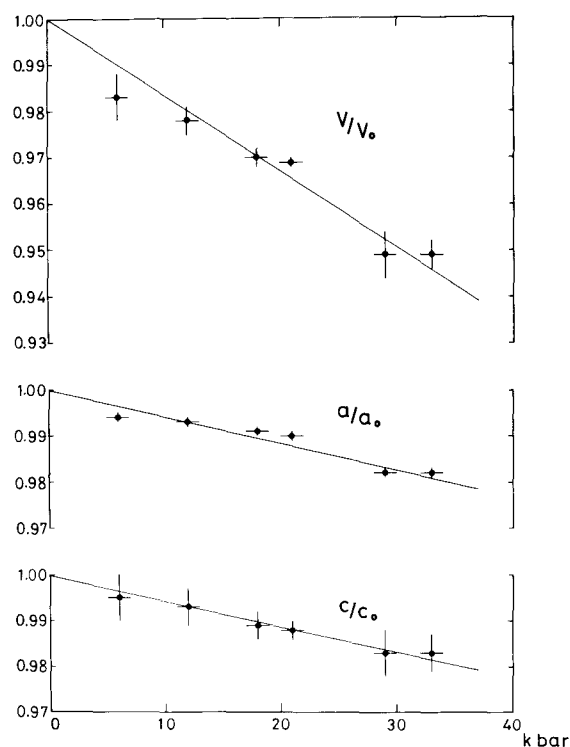


Fig. 1. A plot of relative cell dimensions and cell volume versus pressure

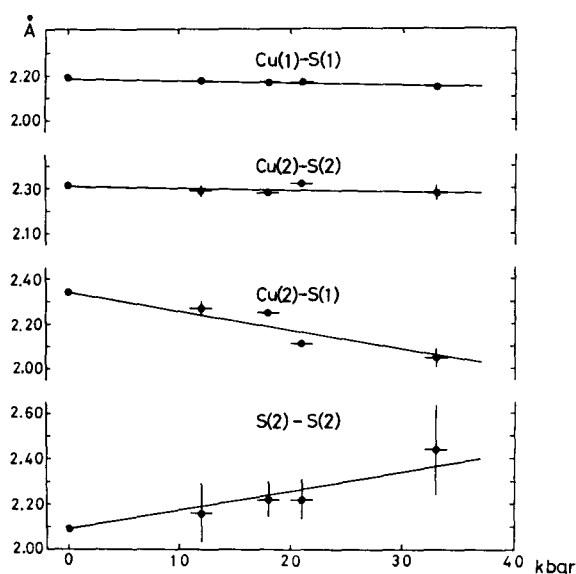
same. It then follows that the axial ratio  $c/a$  is almost invariable up to 33 *kbar* (Table 2). In this figure, we also observe that the compressibility of the cell volume is relatively large, the volume at 1 *bar* being reduced by about 5% at 33 *kbar* (Table 2).

We give in Table 4 some important bond lengths and angles at each pressure, in Figure 2 a plot of bond lengths versus pressure and in Figure 3 links of the Cu–S and S–S bonds. While the triangular area formed by sulfur atoms about Cu(1) contracted by about 2% at 21 *kbar*, the volume of the tetrahedron formed by sulfur atoms about Cu(2) is reduced by about 5.5%. The longest tetrahedral bond, Cu(2)–S(1), in particular, shows a marked contraction (Table 4). These features are in line with the fact that the bond in the triangle is unusually short for three-coordinated copper atoms (Takéuchi and Ozawa, 1975) and stable compared to those in the tetrahedron (Tossell, 1978). By means of X-ray photoelectron spectroscopy, Nakai et al. (1978) showed that both Cu atoms in covellite are monovalent.

It is notable that the sulfur-sulfur distance of the S<sub>2</sub> groups in the structure is lengthened with the increase of pressure, the distance at 21 *kbar*

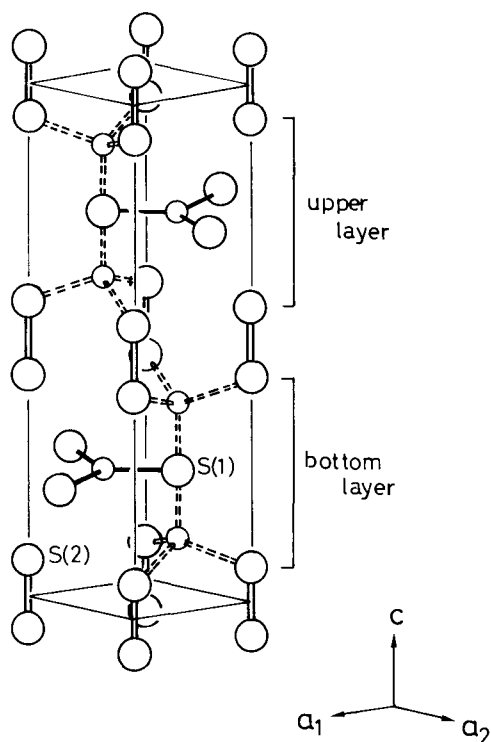
**Table 4.** Selected bond lengths (Å), bond angles ( $^{\circ}$ ), area of the triangle formed by sulfur atoms about Cu(1), and the volume of the tetrahedron formed by sulfur atoms about Cu(2) (those at 1 bar are based on the atomic coordinates given by Ohmasa et al. 1976)

Pressure	1 bar	12 kbar	18 kbar	21 kbar	33 kbar
Triangle					
Cu(1)–S(1) $\times$ 3	2.1915(4)	2.175(2)	2.171(1)	2.169(1)	2.153(1)
Area (Å <sup>2</sup> )	6.239(2)	6.145(7)	6.123(3)	6.111(3)	6.022(7)
Tetrahedron					
Cu(2)–S(1)	2.339(2)	2.27(3)	2.25(1)	2.11(1)	2.05(4)
Cu(2)–S(2) $\times$ 3	2.305(1)	2.29(2)	2.28(1)	2.32(1)	2.28(3)
Average	2.314	2.29	2.27	2.27	2.22
Volume (Å <sup>3</sup> )	6.35(2)	6.1(3)	6.0(1)	6.0(1)	5.6(3)
S(2)–S(2)	2.086(7)	2.16(13)	2.22(8)	2.22(9)	2.44(20)
S(1)–Cu(2)–S(2)	108.04(8)	108(1)	107.6(9)	110.9(8)	109(2)
S(2)–Cu(2)–S(2)	110.87(8)	110(1)	111.2(9)	108.0(9)	109(2)



**Fig. 2.** A plot of bond lengths versus pressure

being expanded by about 6% relative to the value at 1 bar. This situation would probably mean that the contraction of the tetrahedron about Cu(2) induces a delocalization of electrons in the S<sub>2</sub> groups. The pressure dependence of the S–S length of covellite may be compared with the variation of S–S lengths connected with the change of M–S distances in the



**Fig. 3.** The crystal structure of covellite, showing links of the Cu–S and S–S bonds. Large and small circles represent the sulfur and copper atoms, respectively. Heavy solid lines and broken lines indicate the Cu(1)–S and Cu(2)–S bonds, respectively. The double lines show the S–S bonds that connect the bottom and upper layers indicated (see Fig. 5)

structures of the pyrite type,  $MS_2$ , where M represents atoms such as Cu, Ni, Co, Fe or Mn in divalent state. For  $NiS_2$ ,  $CoS_2$  and  $FeS_2$ , the variation of the S–S lengths takes place in such a way that the sum of the two bond lengths, S–S and M–S, is nearly constant (Elliot, 1960). This situation is the same when the corresponding bond lengths of  $CuS_2$  (King and Prewitt, 1979) are taken into account. In Figure 3, we observe that a plot of the S–S bond length versus mean Cu(2)–S distance in covellite shows a trend in a way similar to the above-mentioned mode of variation of S–S versus M–S in  $MS_2$ .

The average value of the S–S distances in the  $CuS_3$  triangle and  $CuS_4$  tetrahedron at 1 bar is calculated to be  $3.783(3)$  Å based on the atomic coordinates given by Ohmasa et al. (1977). This value is reduced to  $3.72(4)$  Å at 21 kbar.

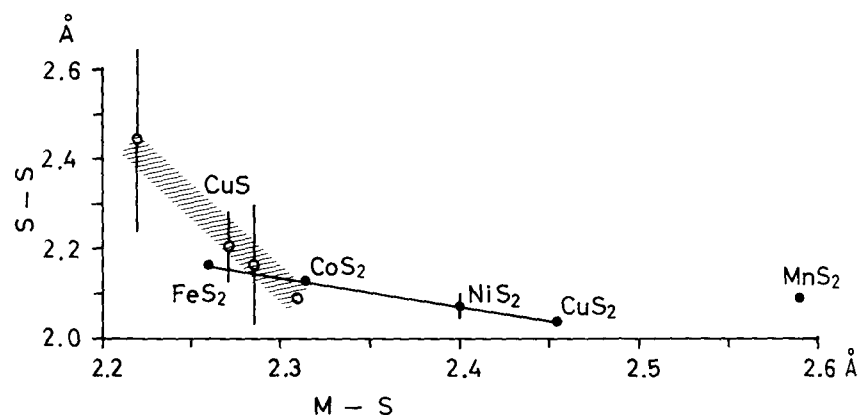


Fig. 4. The variation of the S-S bond lengths of the  $S_2$  groups. *Open circles*: Those of covellite plotted versus mean Cu(2)-S distances. The four entries correspond to the cases of 1 bar, 12 kbar, 21 kbar and 33 kbar from the bottom to the top. *Solid circles*: Those plotted versus metal-sulfur distances for pyrites. The bond lengths of  $MnS_2$  are from Elliot (1960) (sources for others are given in the text)

#### Note on the arrangement of the sulfur atoms in covellite

The fact that the S-S bond length increases with an increase of pressure would suggest the possible existence of a structural transition in CuS at a certain pressure higher than 33 kbar. An inference was then made on the assumed structural change in terms of the arrangement of the sulfur atoms in the structure.

With regard to the sulfur atoms, the unit cell consists of a stack of six sheets of sulfur atoms; in each sheet sulfur atoms are arranged in the fashion of a closest packing. In a way which is conventionally used, we may express the stacking sequence by



The first three symbols denote the sheets in the bottom layer (Fig. 3) and the remainings those in the upper (Fig. 5). Then if the upper layer is shifted by  $x = 1/3$ ,  $y = 2/3$ , the stacking sequence changes to the type of a hexagonal closest packing:



If the shift is  $x = 2/3$ ,  $y = 1/3$ , the resulting sequence becomes



This sequence also represents a closest packing of sheets in which *hcp* and *ccp* types are mixed. If a high-pressure form really existed, the sulfur atoms in the structure would take either one of these types. The shift of layers would be effected by a tilting of the  $S_2$  groups.



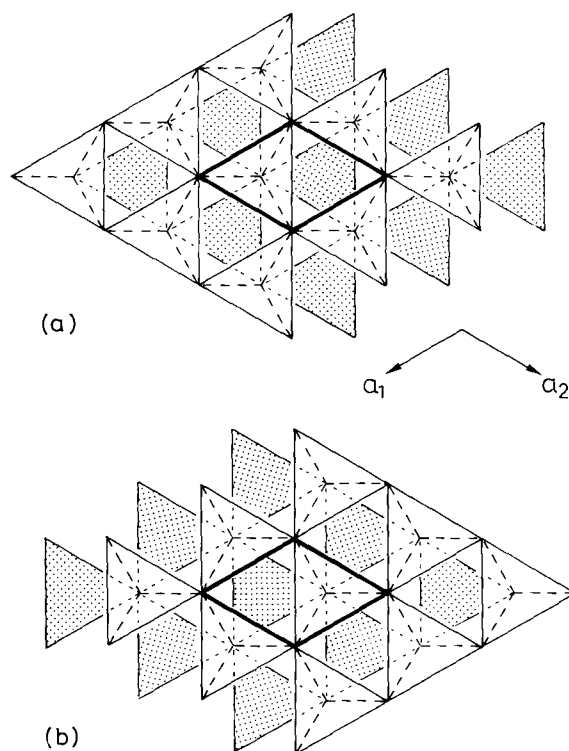


Fig. 5. Polyhedral representation of the layers of covellite viewed down  $c$ , showing upper layer (a) and bottom layer (b) (refer to Fig. 3). Each layer consists of double sheets of tetrahedra about Cu(2) and a sheet of triangles about Cu(1), the latter being stippled. Heavy lines trace the unit cell

#### Addendum

After we completed the manuscript, we became aware of a paper reported by Will et al. (1984). By means of synchrotron X-ray powder diffraction they found that the S–S bonds of the  $S_2$  groups of  $FeS_2$  and  $CoS_2$  are lengthened with an increase of pressure. Although their structure type is different from the CuS type, their result for pyrites is in accordance with the one we observed for CuS.

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