

A refinement of the crystal structure of covellite, CuS

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ABSTRACT

The crystal structure of covellite has been refined, based on counter intensity data, to $R=3.9\%$, using a crystal from Kosaka mine: $P6_3/mmc$, $a=3.976(1)$, $c=16.382(5)\text{\AA}$, $Z=6$. The structure proposed by Oftedal (*Zeits. Krist.*, **83**, 9-25, 1932) was confirmed. The S-S distance of the S_2 groups in the structure is $2.086(7)\text{\AA}$, the Cu-S distance in the CuS_3 triangles $2.1915(4)\text{\AA}$, and the mean Cu-S distances in the CuS_4 tetrahedra 2.313\AA . The highly perfect cleavage characteristic of covellite may well be ascribed to the strong Cu-S bonds in the CuS_3 triangles which form, sharing corners, continuous sheets parallel to (001).

Introduction

The crystal structure of covellite was analyzed by Oftedal (1932). Being composed of CuS_4 tetrahedra, CuS_3 triangles, and links of S-S bonds, the structure is certainly of basic importance in the crystal chemistry of sulfides. A reexamination of the covellite structure carried out by Berry (1954), based on two dimensional photographic data, confirmed the structure proposed by Oftedal, giving improved bond lengths in the structure.

In a paper published elsewhere Takéuchi and Ozawa (1975) made a survey on the Cu-S bond lengths of sulfides in general, and pointed

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out that the Cu-S bond length in the CuS₃ triangles of covellite was unusually short for three-coordinated copper atoms. The present investigation was consequently undertaken in order to establish, by a modern technique, the bond lengths in the structure.

During the course of our study, we happened to be informed by Prof. Wuensch, M. I. T., that a modern refinement of CuS had been done by H. T. Evans, Jr., U. S. Geological Survey. However, we found that bond lengths obtained by Evans (private communication through Prof. Wuensch, 1976) were significantly different from those of the other recent work on covellite (Kalbskopf, Pertlik and Zemann, 1975) which was concurrently came to our attention. Our results reported in the following may serve for assessment of the conflicting results.

Experimental

The specimen used for the investigation came from Kosaka mine, Akita Prefecture, Japan (University Museum, University of Tokyo, No. UTUMMI-00313). The crystals (up to 3 mm wide), being very brittle, were mostly distorted and were not suitable for single crystal works. After a careful search, we finally found a very small platy fragment with dimensions, 0.155 × 0.045 × 0.006 mm, which showed no distortion detectable in X-ray photographs; it was hence used for the following work.

The cell parameters were determined on an automated four-circle diffractometer (Syntex P2₁), using MoK α radiation ($\lambda=0.71069$ Å), monochromatized by a graphite monochromator. They are $a=3.796(1)$ and $c=16.382(5)$ Å, giving a calculated density of 4.66 g·cm⁻³. The ω - 2θ technique was used to measure intensities in one sixth of the hemisphere ($2\theta_{\max}=83^\circ$), including reflections forbidden by the space group. Mean values of F_o 's were calculated after the corrections for Lorentz, polarization and absorption factors. Out of 289 independent reflections, 103 had values less than 1σ ; they were omitted

in the subsequent process of the refinement.

X-ray photographs of covellite showed a hexagonal symmetry and the diffraction symmetry is $P^{**}c$. This permits $P\bar{6}2c$, $P6_3mc$ and $P6_3/mmc$ as possible space groups. Since the observed data agree well to those in the F_o and F_c table published by Berry (1954), $P6_3/mmc$ was assumed to be the correct space group of covellite. The result of the refinement proved that the above assumption was correct.

Refinement of the structure

The refinement was started with the atomic parameters given by Berry (1954). The first structure factor calculations gave the value of $R=0.20$. Several cycles of least-squares calculations by a full-matrix least-squares program, varying anisotropic temperature factors of each atom, reduced the R to 0.078 for all 186 reflections.

As reflections less than 2σ showed still somewhat poorer agreement after the refinement, the parameters were also refined only with the data higher than 2σ . In this case, 125 reflections, this number being more than ten times of the number of the parameters, were used for the least-squares calculations. The R value was then reduced to 0.039. Differences of parameters after the two refinements are within the limits of the standard errors.

For the above calculations, neutral-atom form factors were used taken from International Tables for X-ray Crystallography (1962). Corrections for anomalous dispersion were employed for Cu and S atoms, using the values published by Cromer (1965). Individual weights, $1/\sigma^2(F_o)$, based on counting statistics were used during the course of the refinements. Difference syntheses were computed after each refinement and no anomaly was found in both the cases.

The final atomic coordinates and thermal parameters based on the refinement with 125 data, are given in Table 1 together with the

Table 1. Atomic coordinates and thermal parameters.
Estimated standard errors are in parentheses.

Atom	Position	Berry (1954)	Kalbskopf <i>et al.</i> (1975)	This study
Cu(1)	1/3 2/3 3/4	U_{11} } 0.023	0.015	0.0322(17)
		U_{33} }	0.045	0.0412(14)
Cu(2)	1/3 2/3 z	z	0.1073(3)	0.10724(9)
		U_{11} }	0.023	0.0166(8)
		U_{33} }	0.0147(6)	0.0139(7)
S(1)	1/3 2/3 1/4	U_{11} }	0.023	0.0259(28)
		U_{33} }	0.0180(14)	0.0117(13)
S(2)	0 0 z	z	0.0622(4)	0.0637(2)
		U_{11} }	0.023	0.0115(14)
		U_{33} }	0.0108(10)	0.0096(10)

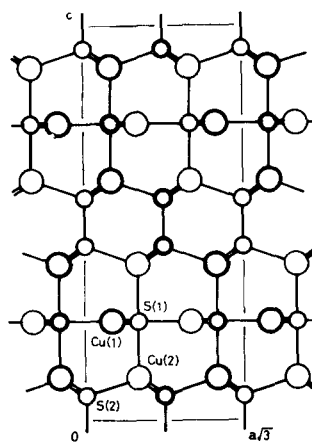


Fig. 1. The structure of covellite projected along a .

results by Berry (1954) and by Kalbskopf *et al.* (1975). Though a strong anisotropy was noted by Kalbskopf *et al.* (1975) of the thermal motion for Cu(1), our results do not show very significant anisotropy of the atom; the component of the root mean square displacements along c is $|\bar{u}|=0.203 \text{ \AA}$, and $|\bar{u}|=0.179 \text{ \AA}$ perpendicular to c . The projection of the structure along the a -axis is depicted in Fig. 1.

Description of the structure and discussions

The structure derived by Oftedal was confirmed, and the atomic coordinates refined by this study are well in accord with those determined by Berry (1954). Interatomic distances and bond angles of covellite calculated with the new coordinates are listed in Table 2, where the values obtained by Berry (1954), Kalbskopf *et al.* (1975), and Evans and Konnert (1976) are also given for comparison. Our bond lengths especially those of S₂ pairs and Cu-S in CuS₃ triangles, are closer to those given by Evans (1976) than those of Kalbskopf *et al.* (1975).

Table 2. Interatomic distances and bond angles.
Estimated standard errors are in parentheses.

	Berry (1954)	Kalbskopf <i>et al.</i> (1975)	Evans* (1976)	This study
Cu(1)-S(1) ($\times 3$)	2.19 Å	2.195(5) Å	2.1905(2) Å	2.1915(4) Å
Cu(2)-S(1)	2.34	2.334(6)	2.331(2)	2.339(2)
Cu(2)-S(2) ($\times 3$)	2.30	2.312(4)	2.305(1)	2.305(1)
S(2)-S(2)	2.09	2.037(11)	2.071(4)	2.086(7)
S(1)-Cu(2)-S(2)	107°	108.6(3)°	108.16(7)°	108.04(8)°
S(2)-Cu(2)-S(2)	111	110.3(3)	110.76(7)	110.87(8)

* After private communication by Prof. B. J. Wuensch.

The S₂ group is surrounded by six copper atoms, which form a distorted octahedron. The S-S distance of the group, 2.086 Å, agrees

well with the single bond length (2.08 Å, Wells, 1962), but is slightly longer than the mean S-S distance (2.06 Å) in the orthorhombic sulfur (Caron and Donohue, 1965). A S-S bond (2.10 Å) is also found in the structure of $\text{Cu}_4\text{Bi}_4\text{S}_9$, in which the S_2 pair is bound to three copper atoms and to a bismuth atom. This distance is slightly longer than that in covellite. The S_2 bonds found in patronite (Kutoglu and Allmann, 1972) are 2.032 and 2.042 Å and considerably shorter than that in covellite. In sulfides and sulfosalts, S-S distances vary in each structure, because difference of ligands effects markedly to S-S length in these materials. For example, S-S distances in the structures of FeS_2 , CoS_2 and NiS_2 , are 2.171, 2.124 and 2.065 Å, respectively (Elliott, 1960).

The arrangement of sulfur atoms around Cu(1) is trigonal and that around Cu(2) is tetrahedral (Fig. 2). These two coordination types are most common in sulfides and sulfosalts. More than twenty structures, containing copper, have been analyzed or refined in the last decade, and Cu-S distances of about seventy Cu polyhedra have been published to date. 39 of them can be assigned as a trigonal coordination, because sums of angles between three shortest bonds are greater than 350° , 25 of them are tetrahedral and the rest non-linear two-fold coordination or similar ones. Fig. 3 indicates the frequency of bonds versus mean bond distances of the trigonal coordination and the tetrahedral coordination. The tetrahedral Cu-S bond of covellite, 2.313 Å, deviates slightly from the most frequent

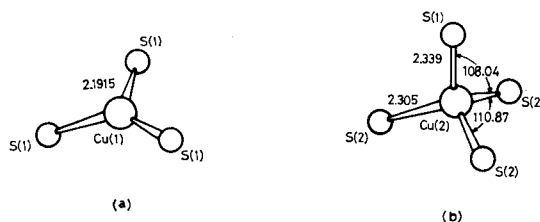


Fig. 2. Coordination around (a) Cu(1), (b) Cu(2).

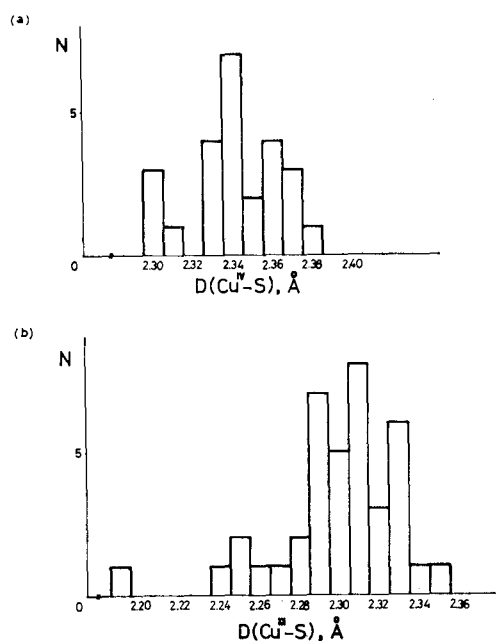


Fig. 3. Frequency of bonds versus mean Cu-S distance.

(a) Cu with tetrahedral coordination.

(b) Cu with trigonal coordination.

distances in Fig. 3a, but the trigonal Cu-S bond, 2.1915 Å, is strikingly shorter than the most frequent region of Fig. 3b. This fact strongly suggests that the Cu(1)-S(1) bond strength should be very large, and the layer formed by Cu(1) and S(1) should be very strong. The highly perfect (001) cleavage of covellite indicates that binding force parallel to (001) is much stronger than that perpendicular to (001). This stronger force parallel to the cleavage plane should be attributed to the short trigonal Cu(1)-S(1) bonds.

Covellite which have some unusual optical properties, was found by Ramdohr (1955) and called "blaubleibender Covellin" or blue remaining covellite. Later works by Frenzel (1959, 1961), by Sillitoe

and Clark (1969) and by Moh (1971) confirmed that the Cu content of blue remaining covellite is rather higher than that of normal covellite and that the formula is expressed as Cu_{1+x}S . In the covellite structure, there is a tetrahedral vacancy formed by three S(1) and one S(2). Although this site is the only one place for excessive Cu, the distance between the center of the vacancy and Cu(1) is too short (2.362 Å) for Cu-Cu contact. The distance between the center and Cu(2) is 2.671 Å. If the Cu-Cu contact of blue remaining covellite is comparable to the shortest Cu-Cu distance of chalcocite (= 2.53 Å, Evans, 1971), and if the position of Cu(1) is same as the Cu(1) position in normal covellite, the unit cell of blue remaining covellite should expand in the *a*- and *c*-directions. X-ray powder photographs of blue remaining covellite given by Moh (1971), shows that all lines are somewhat shifted toward low angle direction. Morimoto and Gyobu (private communication) have also noted from X-ray photographs of single crystal, that the cell of blue remaining covellite is larger than that of normal covellite. These facts may support the above consideration on the distribution of copper atoms in blue remaining covellite.

Versions of the following computer programs were used in this work.

ACACA by C. T. Prewitt (Wuensch and Prewitt, 1965),

ORFLS by W. R. Busing, K. O. Martin and H. A. Levy (1962),

ORFFE by W. R. Busing, K. O. Martin and H. A. Levy (1964).

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