

## Crystal structure refinement of covellite

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### Abstract

The crystal structure of covellite CuS [space group  $P6_3/mmc$ ,  $a = 3.7938(5)\text{\AA}$ ,  $c = 16.341(1)\text{\AA}$ ] has been refined using 237 counter-measured ( $\text{MoK}\alpha$ ) intensity data. The classic structure is confirmed, and  $z$  parameters determined as 0.10733(9) for Cu(2) and 0.06337(15) for S(2). The S-S bond length in the  $S_2$  group is  $2.071(4)\text{\AA}$ , and the Cu-S bond lengths are  $2.1905(2)\text{\AA}$  in the  $\text{CuS}_3$  triangle and  $2.302(1)$  (3 bonds),  $2.331(2)\text{\AA}$  in the  $\text{CuS}_4$  tetrahedron.

### Introduction

The crystal structure of covellite, CuS, was solved 44 years ago by Oftedal (1932). This structure determination is one of the classics of the early era of structure analysis, and the atomic arrangement, although somewhat unusual from a crystal chemical point of view, has been illustrated without further question in countless reviews and textbooks since that time. The first attempt to verify the structure by more modern methods was made by Berry (1954). His study, based on trial and error adjustments using two-dimensional photographic data, served mainly to confirm Oftedal's proposed structure and also, to some degree, to refine it. Bernardini and Catani (1968) again reaffirmed the structure, but used intensities measured from powder patterns, so that our knowledge of the structural details was not much further advanced. Recently, Kalbskopf *et al.* (1975) have reported a new determination based on a least-squares analysis of 59 photographic single-crystal data, giving for the first time reliable interatomic distances in the structure. Unaware of the work of Kalbskopf *et al.*, we have also redetermined the structure of covellite, using 367 independent counter-measured data. Our results are in substantial agreement, but because of the improved data we have been able to attain a considerably higher degree of accuracy.

### Experimental procedure

Covellite grows in soft, thin, hexagonal plates, so that it is difficult to find a crystal sufficiently free of distortion for reliable intensity measurements. The crystal we used, taken from a specimen from Summit-

ville, Colorado, was of good quality as shown by heavily exposed Buerger precession photographs. These photographs showed no trace of any Bragg reflections that would violate the  $c$  glide plane characteristic of the space group  $P6_3/mmc$  (or  $P6_3mc$ ), originally determined by Oftedal (1932). The cell dimensions have been determined by Potter and Evans (1976) by least-squares analysis of powder data to be  $a = 3.7938(5)\text{\AA}$ ,  $c = 16.341(1)\text{\AA}$ . The crystal used for intensity measurement was a plate 0.021 by 0.045 cm in size and 0.00029 cm thick. The scanning profiles were irregular and of varying width, indicating some textural distortions in the crystal, but no peaks were more than  $1^\circ$  in width. With  $\theta$ - $2\theta$  scans of  $3^\circ$  (plus the  $\alpha_1$ - $\alpha_2$  dispersion), the full integrated intensity was effectively registered for all reflections.

All data within one half of the Ewald sphere defined approximately by  $(\sin \theta)/\lambda = 1.0$ , including reflections forbidden by the space group, were measured using Nb-filtered  $\text{MoK}\alpha$  radiation. In fact, because in this structure all atoms are confined to  $x, y$  parameters of 0, 0;  $1/3, 2/3$ ; and  $2/3, 1/3$ , the glide plane extinguishes not only the reflections  $hhl$  with  $l$  odd, but all  $hkl$  reflections with  $h-k = 3n$  and  $l$  odd. None of these reflections showed significant intensity in the measurement, and they have been omitted from further consideration. The total of 1958 reflections (276 forbidden) were reduced by averaging, after corrections were applied, to 367 independent structure amplitudes. Of these, 237 had values greater than  $4\sigma$  on the basis of counting statistics (that is, were above a threshold of  $|F| = 6.2$ ) and were used for the structure analysis.

Absorption corrections were applied to the individually measured reflections using a Gaussian quad-

perature method based on 32 sampling points within the crystal. The calculated linear absorption coefficient, determined from the atomic mass absorption coefficients of Cromer and Liberman (1970), is  $\mu = 165.7 \text{ cm}^{-1}$ . The transmission factors  $A$  varied from 0.35 to 0.95; 75 percent of the measured reflections had  $A$  between 0.85 and 0.95. Of the 367 independent reflections, six equivalent reflections were measured for 162, and three were measured for 190. Thus, a good internal estimate of the standard error of  $|F|$  could be obtained. The overall standard deviation is 2.4. The deviations were uniformly distributed, showed no systematic variation with  $|F|$ , and no connection with low  $A$  values, or any other parameter. On this basis, a minimum  $R$  factor of about 0.05 could be expected. Comparison of the final  $F(\text{obs})$  and  $F(\text{calc})$  values showed no evidence of the influence of secondary extinction, and no correction has been made for it.

The scattering functions for neutral atoms of Doyle and Turner (1968) and the dispersion corrections of Cromer and Liberman (1970) were used in all structure factor calculations. All computations were executed on an IBM370/155 computer using the XRAY72 system edited by J. M. Stewart and co-workers at the University of Maryland.

### Structure analysis

The structure analysis began with Oftedal's structure and proceeded through four stages:

(1) Least-squares refinement in  $P6_3/mmc$  of isotropic atoms, based on 2 variable structure and 4 thermal parameters, led to a conventional reliability factor  $R = 0.072$ .

(2) Least-squares refinement in  $P6_3/mmc$  of anisotropic atoms, based on 2 structure and 8 thermal parameters, led to  $R = 0.054$ .

(3) Least-squares refinement in  $P6_3mc$  of isotropic atoms, based on 5 structure and 6 thermal parameters, led to  $R = 0.058$ .

(4) Least-squares refinement in  $P6_3mc$  of anisotropic atoms, based on 5 structure and 12 thermal parameters, led to  $R = 0.045$ .

The convergence of runs 1 and 2 was smooth and secure. It is surprising to find a considerable improvement in  $R$  in proceeding from 2 to 4, but in runs 3 and 4 the convergence is unstable. In both the last two cases, correlation factors greater than 0.95 were encountered, especially between the  $z$  parameters of the atom pairs originally related by the mirror plane. The noncentrosymmetric analysis therefore cannot be considered reliable.

Kalbskopf *et al.* (1975) suspected that the prolate anisotropy of thermal motion for Cu(1) which they found, and which has also been observed by us (Fig. 1), might actually represent a configuration in which this atom is at the vertex of a low pyramid with respect to the coordinated triangle of S(2) atoms. We also tested this hypothesis, as they did, by placing 1/2 Cu(1) at 0.24, and continuing least-squares analysis. Keeping this atom isotropic, 2 cycles led to  $U = 0.029(1)\text{\AA}^2$  and  $z = 0.2435(5)$  ( $0.106(8)\text{\AA}$  from the mirror plane) for Cu(1), with a correlation ratio of 0.64 for these 2 parameters. In 2 cycles of anisotropic refinement, this atom attained  $U_{33} = 0.031(13)\text{\AA}^2$  and  $z = 0.2439(34)$ , with a correlation ratio of 0.991. In both refinements the reliability factor remained at  $R = 0.054$ .

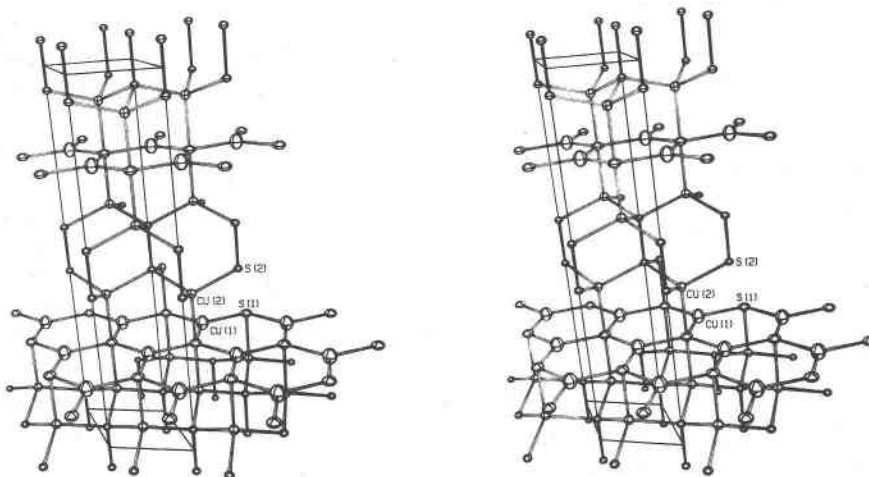


FIG. 1. Stereoscopic view of the crystal structure of covellite. The thermal ellipsoids represent the 50 percent probability surfaces.

Thus, no valid evidence can be found for either a noncentrosymmetric or a split-atom model for covellite. The results of the anisotropic centrosymmetric refinement (stage 2 above) must therefore be accepted as the best. These results are shown in Table 1 compared with the parameters obtained in previous structure studies. The structure factors are listed in Table 2 (in this table,  $|F(\text{obs})|$  is left blank when its measured value falls below  $4\sigma$ ).

The possibility of the existence of a homometric structure (that is, a wholly different arrangement that would yield the same structure amplitudes as the classic structure) was explored. Many different arrangements both in  $P6_3/mmc$  and  $P6_3mc$ , especially those based on close-packed sulfur atoms in ABCACB stacking, were tested without finding any that would give  $R < 0.3$ . Such a possibility now seems extremely unlikely.

A  $\Delta F$  Fourier synthesis containing 85 terms for which  $(\sin \theta)/\lambda < 0.4$  showed maxima of 0.4 electron  $(e)/\text{\AA}^3$  at 1/3, 2/3, 0.145 and 0.3  $(e)/\text{\AA}^3$  at 2/3, 1/2, 1/4; also minima of  $-0.6 (e)/\text{\AA}^3$  at 2/3, 1/3, 0.116 and  $-0.4 (e)/\text{\AA}^3$  at 0, 0, 1/4. There appears to be no reasonable explanation for these features, and we regard them as spurious.

### The crystal structure

Covellite has an unusual structure for such simple stoichiometry as  $\text{CuS}$ . Of the 6 formula units in the unit cell, 4 of the Cu atoms have tetrahedral and 2 triangular coordination; 4 of the S atoms form disulfide  $\text{S}_2$  groups, and 2 are single sulfide ions. The structure is illustrated in a stereoscopic drawing showing the thermal ellipsoids in Figure 1. Bond lengths and angles are shown in Figure 2.

TABLE 1. Structural and thermal parameters for covellite

Atom	Parameters	This work	Kalbskopf et al. (1975)	Berry (1954)
Structural parameters:				
Cu(1)	x, y, z	2/3, 1/3, 1/4	2/3, 1/3, 1/4	2/3, 1/3, 1/4
Cu(2)	x, y	1/3, 2/3	1/3, 2/3	1/3, 2/3
	z	0.10733(9)	0.1073(3)	0.107
S(1)	x, y, z	1/3, 2/3, 1/4	1/3, 2/3, 1/4	1/3, 2/3, 1/4
S(2)	x, y	0, 0	0, 0	0, 0
	z	0.06337(15)	0.0624(8)	0.064
Thermal parameters (in $\text{\AA}^2$ ):				
Cu(1)	$U_{11}(U)$	0.0289(10)	0.015	} 0.023
	$U_{33}(U)$	0.0414(17)	0.045	
Cu(2)	$U_{11}(U)$	0.0142(4)	0.0147(6)	
	$U_{33}(U)$	0.0135(5)		
S(1)	$U_{11}(U)$	0.0255(15)	0.0180(14)	
	$U_{33}(U)$	0.0100(13)		
S(2)	$U_{11}(U)$	0.0117(6)	0.0108(10)	
	$U_{33}(U)$	0.0069(8)		

The  $\text{S}_2$  group has a bond strength of 2.071(4) $\text{\AA}$ , which is considerably shorter than those found in the polymorphs of  $\text{FeS}_2$  by Brostigen and Kjekshus (1969), 2.177(4) in pyrite and 2.223(3) $\text{\AA}$  in marcasite; but longer than 2.042(3) $\text{\AA}$  and 2.032(3) $\text{\AA}$  as found in patronite  $\text{V}(\text{S}_2)_2$  by Allmann *et al.* (1964). The average bond length in the Cu(2) tetrahedron is 2.312 $\text{\AA}$ , slightly larger than the best recent determinations of tetrahedral Cu-S bond lengths: 2.302(1) $\text{\AA}$  in chalcocopyrite (Hall and Stewart, 1973) and 2.305 $\text{\AA}$  in cubanite (average; Szymanski, 1974). The Cu(1)-S(2) bond lengths of 2.1905(2) $\text{\AA}$  in the triangular group are considerably less than the average value of 2.33 $\text{\AA}$  found for 24 independent  $\text{CuS}_3$  triangles in low-chalcocite by Evans (1971).

The thermal motion is markedly varying and anisotropic for the different atoms in covellite (Fig. 1), but the anisotropy is largely what would be expected, considering the surroundings of each atom. Thus, the triangular Cu(1) has a large motion along  $c$  [ $\bar{u} = 0.203(4)\text{\AA}$ ], where no other atoms offer any serious restraint [the nearest Cu(2) atom is at a distance of 3.199(1) $\text{\AA}$ ]. Along the Cu-S bond  $\bar{u} = 0.170(3)\text{\AA}$ , similar to the corresponding motion of S(1), for which  $\bar{u} = 0.160(2)\text{\AA}$ . The S(1) atom, held between two Cu(2) atoms, has  $\bar{u} = 0.100(6)\text{\AA}$  along these bonds ( $c$  axis). The tetrahedral Cu(2) is practically isotropic, with  $\bar{u} = 0.118(2)\text{\AA}$ . In the  $\text{S}_2$  group, S(1) has  $\bar{u} = 0.109(2)\text{\AA}$  normal to the S-S bond, and  $\bar{u} = 0.083(5)\text{\AA}$  along the bond.

While tetrahedral coordination for copper in sulfides is common, triangular coordination has been found in only a few species. Lewis and Kupcik (1974) listed 5 (low-chalcocite, wittichenite, anilite, hod-rushite, and synthetic  $\text{Bi}_2\text{Cu}_3\text{S}_4\text{Cl}$ ) to which must be added covellite, stromeyerite,  $\text{AgCuS}$  (Frueh, 1955), tetrahedrite,  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  (Wuensch, 1964), bornite,  $\text{Cu}_5\text{FeS}_4$  (Koto and Morimoto, 1975), and synthetic  $\text{Cu}_4\text{Bi}_4\text{S}_9$  (Takeuchi and Ozawa, 1975). The last compound ( $\text{Cu}_4\text{Bi}_4\text{S}_9$ ) contains  $\text{S}_2$  groups and linkages of  $\text{CuS}_4$  tetrahedra and  $\text{CuS}_3$  triangles resembling those seen in portions of the covellite structure. Covellite contains a continuous layer of S atoms in triangular array with every other triangle occupied by a Cu atom. An exactly similar layer is present in stromeyerite, and similar but interrupted layers also appear in low-chalcocite (Evans, 1971). Evidently this arrangement is characteristic of metal sulfides rich in copper and may be expected to appear in other complex copper sulfide phases.

A rigorous discussion of the electronic and bonding characters of the covellite structure is beyond the

TABLE 2. Observed and calculated structure factors for covellite

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
0	0	2	19.6	19.0	2	0	6	17.1	16.9	1	3	52.1	51.6	3	1	27	27.0	28.9	
0	0	4	20.1	18.2	2	0	7	43.2	42.7	4	1	8.4	7.1	3	1	28	8.2	5.4	
0	0	6	157.4	158.2	2	0	8	65.7	65.4	4	1	16.2	18.3	4	1	0	49.4	15.3	
0	0	8	68.9	69.0	2	0	9	19.7	17.5	4	1	11.3	10.8	4	1	2	7.2	17.1	
0	0	10	26.2	4.7	2	0	10	24.4	26.2	4	1	35.5	35.1	4	1	4	9.2	0.8	
0	0	12	26.2	25.3	2	0	11	43.7	43.0	4	1	52.7	53.7	4	1	6	33.5	9.8	
0	0	14	63.2	62.1	2	0	12	18.5	19.9	4	1	12.1	13.0	4	1	8	9.0	23.1	
0	0	16	41.2	44.0	2	0	13	18.5	19.9	4	1	22.0	23.2	4	1	10	21.2	9.7	
0	0	18	28.8	28.1	2	0	14	45.3	48.7	4	1	34.0	34.5	4	1	12	9.1	11.2	
0	0	20	31.8	32.7	2	0	15	19.1	19.5	4	1	16.9	17.0	4	1	14	15.0	11.7	
0	0	22	43.9	43.9	2	0	16	14.7	16.0	4	1	40.1	41.1	4	1	16	11.3	3.2	
0	0	24	24.0	24.9	2	0	17	23.3	24.1	4	1	15.3	16.7	4	1	18	9.1	2.3	
0	0	26	11.3	11.9	2	0	18	6.5	6.5	4	1	16.2	15.0	4	1	20	10.7	7.3	
0	0	28	23.5	23.8	2	0	19	4.3	4.4	4	1	12.2	12.2	4	1	22	16.2	11.6	
0	0	30	10.1	5.6	2	0	20	15.9	15.5	4	1	19.6	20.3	4	1	24	13.9	1.9	
1	0	0	38.0	38.4	2	0	21	21.2	22.2	5	0	18	3.7	5	1	0	1.8	1.0	
1	0	1	33.9	32.5	2	0	22	1.1	1.1	5	0	7	15.7	14.6	2	1	8.8	7.2	
1	0	2	61.6	58.1	2	0	23	1.1	1.1	5	0	8	20.9	22.3	2	1	2	8.2	9.6
1	0	3	98.6	94.1	2	0	24	9.5	9.5	5	0	9	18.9	19.3	5	1	3	12.1	8.1
1	0	4	8.1	8.1	2	0	25	11.6	10.9	5	0	11	1.4	5	1	4	3.8	3.7	
1	0	5	36.0	35.2	2	0	26	6.0	6.0	5	0	11	1.1	5	1	5	3.7	10.5	
1	0	6	25.8	25.6	2	0	27	11.7	9.3	5	0	12	10.6	8.4	5	1	6	1.4	4.1
1	0	7	55.5	54.3	2	0	28	9.5	7.5	5	0	13	6.8	7.7	2	1	25	11.1	8.1
1	0	8	84.7	83.8	2	0	29	9.5	9.1	5	0	14	15.5	18.0	2	1	26	9.4	5.7
1	0	9	23.4	24.3	2	0	30	8.4	8.4	5	0	15	10.6	6.5	5	1	27	10.0	6.2
1	0	10	28.5	30.3	3	0	0	100.2	105.0	5	0	16	10.1	9.6	2	1	28	11.6	14.4
1	0	11	55.2	55.9	3	0	2	0.7	0.7	5	0	17	9.2	9.4	2	1	29	11.6	13.0
1	0	12	7.1	8.5	3	0	4	15.1	14.9	5	0	18	9.2	2.5	2	1	30	11.5	4.3
1	0	13	21.4	23.5	3	0	6	68.8	76.0	5	0	19	1.9	2	1	31	10.8	16.1	
1	0	14	56.7	58.7	3	0	8	24.9	24.3	6	0	2	23.0	26.6	2	1	32	10.3	11.6
1	0	15	22.6	23.0	3	0	10	2.7	2.7	6	0	2	6.2	6.3	5	1	15	6.2	0.0
1	0	16	16.3	16.9	3	0	12	11.8	10.9	6	0	4	15.1	15.0	5	1	16	10.1	8.9
1	0	17	29.0	29.1	3	0	14	29.3	29.5	6	0	1	21.6	21.6	5	1	17	11.8	6.9
1	0	18	7.4	7.4	3	0	16	20.9	24.9	1	1	3	32.1	32.5	5	1	18	7.6	13.6
1	0	19	17.0	18.5	3	0	18	18.8	20.8	1	1	4	8.2	5.8	2	2	0	86.9	8.8
1	0	20	25.9	25.8	3	0	20	15.7	18.9	1	1	5	10.0	10.7	2	2	4	12.5	8.4
1	0	21	1.0	1.0	3	0	22	25.4	28.4	1	1	6	4.0	4.0	2	2	6	57.7	2.2
1	0	22	1.0	1.0	3	0	24	17.6	17.2	1	1	7	24.7	25.2	2	2	8	16.1	17.8
1	0	23	1.0	1.0	3	0	26	7.4	7.4	1	1	8	36.7	36.6	2	2	6	16.1	17.8
1	0	24	6.5	10.6	3	0	28	16.1	16.1	1	1	9	9.1	7.9	2	2	10	9.0	8.3
1	0	25	12.6	12.2	4	0	0	9.3	9.7	1	1	14	17.7	18.7	2	2	12	2.3	2.3
1	0	26	11.9	6.3	4	0	1	12.7	13.1	3	1	11	22.1	23.4	2	2	14	23.5	23.8
1	0	27	11.9	11.3	4	0	2	17.5	18.5	1	1	12	2.0	2.0	2	2	16	19.3	21.5
1	0	28	10.1	8.7	4	0	3	26.3	26.6	1	1	13	12.4	12.8	2	2	18	17.7	19.0
1	0	29	11.2	10.4	4	0	4	9.0	5.4	1	1	14	29.4	30.5	2	2	20	16.2	16.0
1	0	30	9.5	9.5	4	0	5	9.0	8.6	1	1	15	12.2	12.5	2	2	22	23.1	24.8
1	0	31	6.4	6.4	4	0	6	26.9	27.0	1	1	16	10.9	13.0	2	2	24	17.9	17.7
1	0	32	10.8	11.3	4	0	7	20.4	21.7	1	1	17	14.7	15.1	2	2	26	6.4	6.4
2	0	0	26.5	25.6	4	0	8	31.4	33.3	1	1	18	4.3	4.3	2	2	28	14.4	14.3
2	0	1	24.7	23.9	4	0	9	6.4	6.4	1	1	19	2.8	2.8	3	2	0	11.7	11.5
2	0	2	40.2	39.1	4	0	10	16.1	16.9	1	1	20	9.4	9.7	3	2	2	15.6	15.9
2	0	3	68.9	68.4	4	0	11	18.6	19.9	2	1	21	14.4	14.8	3	2	4	21.6	22.5
2	0	4	7.2	8.0	4	0	12	1.3	1.3	2	1	22	1.6	1.6	3	2	6	5.0	5.0
2	0	5	25.7	25.2	4	0	13	12.4	11.2	2	1	23	10.4	6.6	3	2	8	8.4	7.0
2	0	6	13.7	13.7	4	0	14	10.4	8.1	3	1	24	10.4	6.6	3	2	5	8.4	7.0
2	0	7	12.0	13.7	4	0	15	10.4	8.1	3	1	25	10.4	6.6	3	2	7	18.1	18.9
2	0	8	11.2	11.8	4	0	16	9.2	9.2	3	1	26	9.2	5.0	3	2	6	11.2	11.8

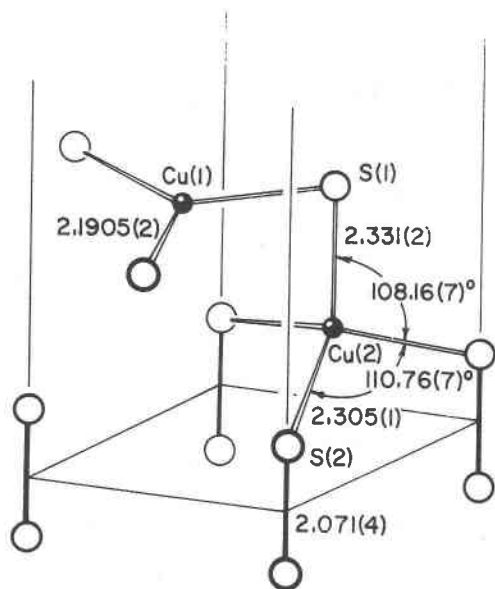


FIG. 2. Portion of the covellite structure showing bond lengths (in Å) and angles. Numbers in parentheses represent standard deviations in terms of last significant figures.

scope of this paper, but one or two empirical observations may be made. Clearly, the strong bond in the  $S_2$  group requires that the average valence of Cu be considerably less than 2. If the average triangular bond in low-chalcocite,  $Cu_2S$ , is  $2.33\text{Å}$  (Evans, 1971) we may hypothesize that this distance corresponds to a bond number of  $1/3$ . Then, Cu(2) in covellite should have a total valence of slightly more than  $4/3$ . If S(1) is assumed to have a valence of 2, then it follows that Cu(1) also will have a valence of  $4/3$ . According to Pearson's extension of the 8- $N$  rule (Pearson, 1964), the number of valence electrons  $n_e$  and the number of electrons involved in anion-anion bonding  $b_a$  should satisfy the relation  $(n_e + b_a)/n_a = 8$ , where  $n_a$  is the number of cations. Applying this rule to covellite,  $Cu_3S(S_2)$ , we find that it is satisfied (when  $b_a = 2$ ) only if the 3 Cu atoms contribute 4 electrons. This is consistent with the interpretation of the bond lengths given above.

Evidently the perfect (001) cleavage of covellite results from the fact that there is one  $1/3$  bond in the  $CuS_4$  tetrahedron parallel to the  $c$  axis, which is the only bond in the unit cell holding the structure together in this direction.

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