

## REFINEMENT OF THE STRUCTURE OF SULVANITE

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## ABSTRACT

The structure of sulvanite,  $\text{Cu}_3\text{VS}_4$  was solved by Pauling and Hultgren (1933). The bonding of V to S is an unusual one which, it was thought, warranted checking and refining the structure. The crystals have symmetry  $P\bar{4}3m$ , with  $a=5.3912\pm 0.0007$  Å. Pauling and Hultgren's structure was confirmed and refined by least squares. The new value of the positional parameter of S is  $x=0.2372\pm 0.0003$ , which leads to a V-S distance of 2.214 Å and Cu-S distance of 2.297 Å.

## INTRODUCTION

The crystal structure of sulvanite was first investigated by de Jong (1928) by means of powder photographs. His structure was based upon a cubic cell with  $a=10.772$  Å and containing eight  $\text{Cu}_3\text{VS}_4$ . Later Pauling and Hultgren (1933) pointed out that the experimental data published by de Jong did not necessarily lead to such a large cell edge. With Laue and oscillation photographs, they showed that the cell edge is  $a=5.386$  Å and contains only one  $\text{Cu}_3\text{VS}_4$ . The space group was determined as  $P\bar{4}3m$ .

## DATA COLLECTION

The experimental work reported here was done with a specimen from Mercur, Utah, kindly provided by Professor Clifford Frondel from the Harvard Museum collection. An accurate value of the cell edge was determined by the use of a back-reflection Weissenberg photograph. The result,  $a=5.3912\pm 0.0007$  Å, is consistent with values 5.390 Å found by Lundquist and Westgren (1936) and 5.391 Å, by Berry and Thompson (1962). The space group,  $P\bar{4}3m$ , determined from Friedel symmetry of the precession photographs and the tetrahedral habit, is the same as reported by Pauling and Hultgren (1933).

A rectangular crystal with the dimensions  $0.207\times 0.105\times 0.057$  mm was selected for intensity measurements. Integrated intensities were collected by means of an equi-inclination diffractometer using Zr-filtered  $\text{MoK}\alpha$  radiation. Precise adjustments on the diffractometer assured that the whole crystal was within the cross section of constant intensity of the  $x$ -ray beam, and care was taken not to exceed the linearity range of the scintillation detector. Despite the small size of the crystal, the difference in the transmission factors between the shortest and longest path of the  $x$ -ray beam through the crystal was about 10%. Accordingly, the measured intensities were corrected for absorption as well as Lorentz and polarization factors.

## REFINEMENT

A Patterson map immediately indicated that a sphalerite-type structure is not possible for sulvanite, a conclusion reached on other grounds by Pauling and Hultgren. A preliminary set of structure factors was calculated using the coordinates found by Pauling and Hultgren, listed in Table 1. The signs from the set of  $F_{\text{cal}}$  were attributed to  $F_{\text{obs}}$ , and with these Fourier coefficients a three-dimensional electron-density map was computed using the IBM 7094 program MIFR 2 written by Shoemaker (1965), unpublished. With a preliminary scale factor and isotropic temperature factors, the discrepancy factor  $R$ , was 18.3%. This  $R$  value and the electron-density map were sufficient to show that the structure obtained by Pauling and Hultgren was substantially correct.

TABLE 1. ATOMIC PARAMETERS OF SULVANITE

Atom	Equipoint	Coordinates	$x$	$\sigma(x)$	$B$	$\sigma(B)$
V	1a	000			0.395 Å <sup>2</sup>	0.032 Å <sup>2</sup>
Cu	3d	$\frac{1}{2}$ 00			1.258	0.030
S	4e	xxx	0.2372	0.0003	1.019	0.031
Pauling and Hultgren: 0.235						

A least-squares refinement of these preliminary results was carried out with the SFLSQ 3 program written by C. T. Prewitt (see Onken, 1964). Several cycles of refinement, allowing all parameters to vary, led to an  $R$  value of 12.4%. Attempts to decrease this residual, such as by using anisotropic temperature factors, failed to improve  $R$ . Since a difference synthesis suggested that the Cu atom had considerable anisotropic thermal motion, an attempt was also made to represent it by four fractional atoms (Kantha and Ahmed, 1960). This also did not reduce  $R$ .

An improved set of data was obtained making appropriate corrections for background. With these new data the unweighted  $R$  dropped to 10.6% and the weighted  $R$  to 5.8%. Introducing anisotropic thermal parameters gave a final  $R=9.8\%$  (unweighted) and  $R=5.2\%$  (weighted). The difference between the last two residual values shows that the agreement between  $|F_{\text{obs}}|$  and  $|F_{\text{cal}}|$  for weak intensities is a rather poor one.

## DISCUSSION OF THE STRUCTURE

The refinement confirmed the atomic arrangement for sulvanite as reported by Pauling and Hultgren, and improved it by a small shift of the coordinates of the sulfur atom. The final atomic parameters are

TABLE 2. INTERATOMIC DISTANCES AND BOND ANGLES BETWEEN ATOMS IN SULVANITE

Atoms	Interatomic distances	Angles	$\sigma$
V-S	2.2149 Å		0.0009
Cu-S	2.2973 Å		0.0008
V-Cu	2.6956 Å		—
S(xxx)-V(000)-S( $\bar{x}\bar{x}x$ )		109°28'	0.11
S( $\bar{x}\bar{x}x$ )-Cu( $\frac{1}{2}$ 00)-S( $\bar{x}x\bar{x}$ )		103°51'	0.10
S(xxx)-Cu( $\frac{1}{2}$ 00)-S( $\bar{x}\bar{x}x$ )		112°21'	0.04

listed in Table 1; the interatomic distances and the bond angles in Table 2. The anisotropic temperature coefficients computed by the least-squares refinement are presented in Table 3. The symmetry relations of these coefficients were calculated according to Levy (1956) and Trueblood (1956).

Both V and Cu are tetrahedrally coordinated to S. The tetrahedron about V is a regular tetrahedron with the angle S-V-S = 109°28', while that about Cu is somewhat distorted with S-Cu-S = 103°51' and 112°21'. The S atom is surrounded by three Cu atoms situated at the middle of the cell edge, and by a V atom located at the origin; thus S has coordinating neighbours only on one side. The interatomic distances are similar to those reported for other structures. The Cu-S distance, 2.297 Å, is in fair agreement with values 2.28 Å listed by Wuensch and Buerger (1963) on chalcocite and 2.342 Å, 2.272 Å determined by Wuensch (1964) on tetrahedrite. The V-S distance, 2.214 Å, is about 0.1 Å shorter than V-S distances of 2.32 Å and 2.31 Å obtained by Pedersen and Grønvdold (1959) on  $\alpha$  V<sub>3</sub>S and  $\beta$  V<sub>3</sub>S.

In order to study the possible thermal motion of the sulfur atom in its unusual coordination, a three-dimensional difference map was com-

TABLE 3. ANISOTROPIC TEMPERATURE COEFFICIENTS FOR THE ATOMS IN SULVANITE

Atom	Symmetry	Symmetry restriction	$\beta$ values	$\sigma(\beta)$
V	$\bar{4}3m$	$\beta_{11} = \beta_{22} = \beta_{33}$ $\beta_{12} = \beta_{23} = \beta_{13} = 0$	$\beta_{11} = 0.0036$	0.0002
Cu	$\bar{4}2m$	$\beta_{11} = \beta_{22} = \beta_{33}$ $\beta_{12} = \beta_{23} = \beta_{13} = 0$	$\beta_{11} = 0.0081$ $\beta_{22} = 0.0122$	0.0004 0.0003
S	$3m$	$\beta_{11} = \beta_{22} = \beta_{33}$ $\beta_{12} = \beta_{23} = \beta_{13}$	$\beta_{11} = 0.0088$ $\beta_{12} = 0.0018$	0.0002 0.0005

puted, based upon the structure refined with anisotropic thermal parameters. Two sections of this are shown in Fig. 1*b* and 1*c*, related to each other as illustrated in Fig. 1*a*. If the difference shown in Fig. 1*b* and 1*c*, which represents about 1.2 electrons of the sulfur atom, can be regarded as significant, it appears that the sulfur atom cannot be represented by

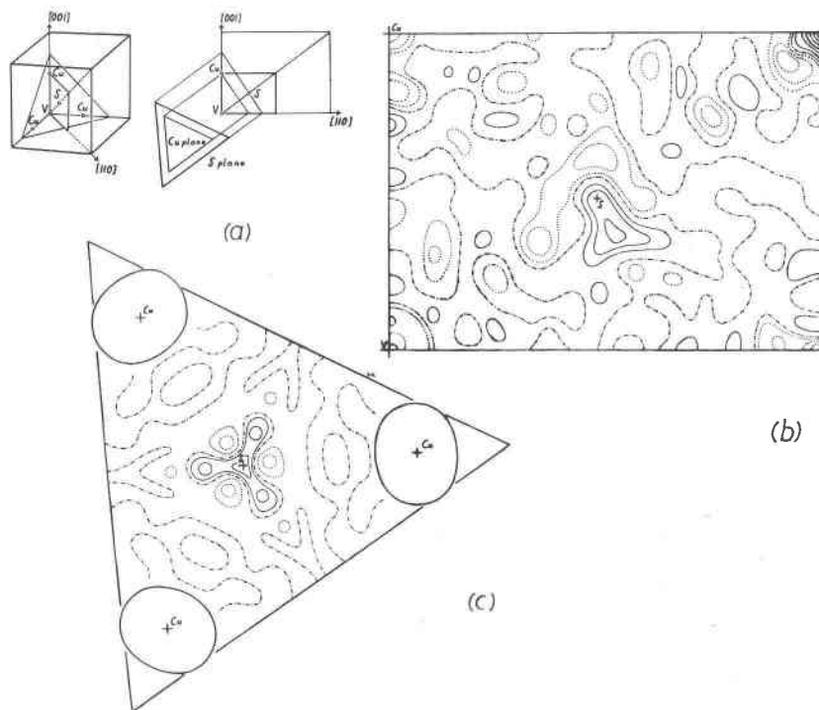


FIG. 1. Electron-density difference map for sulvanite; (a) orientation of the sections with respect to the unit cell; (b) section along (110). (c) section parallel to (111) on which the copper peaks from the density map are projected. Contours at equal but arbitrary intervals, the negative contours are dotted, the zero contour is dash-dotted, and the positive contours are solid lines.

a spherical electron-density distribution modified by an elliptical thermal motion. The maps may be interpreted as suggesting that there are displacements directed into the empty space between pairs of the three nearest Cu neighbours. Such displacements could represent anharmonic thermal motion or static disorder; an attempt to split the S atom into three fractional atoms did not improve the *R* factor.

The V atom at the origin appears as a very sharp peak and has a low temperature factor. On the other hand, the peak representing Cu is

smearred and of abnormally low height, indicating a thermal motion which, as the difference map shows in this case, can be represented by an ellipsoid. According to the anisotropic temperature-factor coefficients listed in Table 3, the Cu atom has a higher thermal displacement perpendicular to the  $\bar{4}$  axis than parallel to it.

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