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THE CRYSTAL STRUCTURE OF CHALCOCITE, Cu_2S

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ABSTRACT

The crystal structures of the high- and low-temperature forms of Bristol, Conn., chalcocite have been investigated with single-crystal methods. At 125° C., high-chalcocite has lattice constants $a=3.95$ and $c=6.75$ Å, and space group $P6_3/mmc$. The sulfur atoms are arranged in hexagonal close-packing. The copper atoms are disordered. The most satisfactory approximation to the structure contains Cu atoms statistically distributed in three types of sites. Cu' is in three-fold coordination and forms of trigonal Cu-S layer. Cu'' occupies the tetrahedral interstices. Cu''' is in two-fold coordination and links S atoms in neighboring Cu-S sheets.

All electron density in the low-chalcocite substructure is confined to locations corresponding to positions on the 3-fold or 6-fold axes of high-chalcocite. A structure similar to that of stromeyerite, CuAgS, may be derived from that of high-chalcocite by appropriate displacements of the copper atoms. The low-chalcocite structure is very likely a similar derivative structure.

INTRODUCTION

Until about twenty years ago, it was believed that chalcocite, Cu_2S, was dimorphous and existed in orthorhombic and isometric modifications. N. W. Buerger (1941), however, showed that while chalcocite was indeed orthorhombic below about 110° C, stoichiometric Cu_2S actually transformed to a hexagonal phase. Compositions deficient in copper, on the other hand, transformed into this hexagonal phase plus an isometric phase. The isometric structure had composition near Cu_9S_5 and was shown to be identical with what had been called isometric chalcocite (N. W. Buerger, 1942). The name digenite was proposed for this cubic modification. Electrical conductivity measurements (Hirahara, 1947) indicated a further phase transition in Cu_2S at 450° C. Ueda (1949) found that this new phase was similar to digenite. In a careful re-examination of the phase relations in the system, Djurle (1958*a*) confirmed this transformation, but, in addition, discovered two new phases at composition $Cu_{1.96}S$. At room temperature crystals of this composition had an unidentifiable structure of low symmetry. At higher temperatures a relatively simple metastable tetragonal structure was formed. It was found that all compositions between Cu_2S and $Cu_{1.8}S$ transformed into a digenite-like phase at a sufficiently high temperature. Dignite may therefore be described as $Cu_{2-x}S$ with x between 0 and at least 0.2.

The nomenclature "low-chalcocite" and "high-chalcocite" will be preserved in this paper for the orthorhombic and hexagonal modifications, respectively, of stoichiometric Cu_2S. The two phases are related by a reversible transformation. The high-temperature form cannot be quenched. M. J. Buerger and N. W. Buerger (1944) showed that an interesting substructure-superstructure relation exists between the unit cells of the two structures. The diffraction patterns of low-chalcocite contained weak reflections in addition to those displayed by the hexagonal form. These additional reflections indicated that the axes of the low-chalcocite unit cell were multiples of 3, 4 and 2 of the cell edges of the orthohexagonal cell of high-chalcocite in the a, b and c directions respectively. This relation is illustrated in Fig. 1, in which the lattice points of the A-centered low-chalcocite cell are given by solid points and the lattice points of the hexagonal high-chalcocite cell by open points. The diffraction symbol for high-chalcocite permitted $P6_3mc$, $P3/m2c$ and $P6_3/mmc$ as possible space groups; low-chalcocite had $Abmm$, $Ab2m$ and $Abm2$ as possible space groups. By assuming that the space

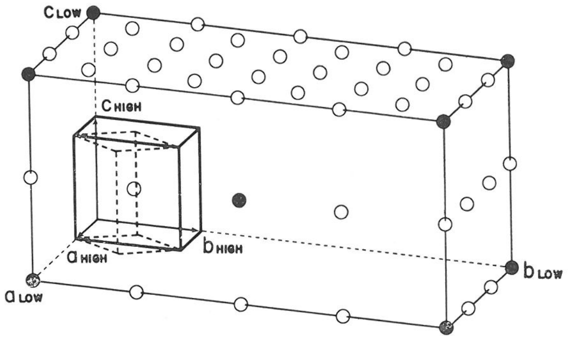

FIG. 1. Relation between the orthohexagonal unit cell of high-chalcocite and the A-centered orthorhombic unit cell of low-chalcocite. The lattice points of high-chalcocite are indicated by open points, and those of low-chalcocite by solid points. The hexagonal cell of high-chalcocite is indicated by heavy dotted lines.

group of low-chalcocite was derived from that of high-chalcocite through the suppression of certain symmetry elements, it was possible to assign space group $Ab2m$ (C_{2V}^{15}) to low-chalcocite, and space group $P6_3/mmc$ (D_{6h}^{4}) to high-chalcocite. The acentric orthorhombic structure contains 96 Cu_2S per unit cell and is quite complex. The hexagonal cell of high-chalcocite, on the other hand, contains only 2 Cu_2S per cell.

An attempt to solve the relatively simple high-chalcocite structure from powder data (Klubock and Buerger, 1945, unpublished) was unsuccessful. Belov and Butuzov (1946), however, considered the several reasonable structures permitted by the high-chalcocite space group. They proposed as a structure that model which gave the best fit with a set of intensities estimated from a high-chalcocite Weissenberg photograph published by Buerger and Buerger (1944). The agreement was rather unsatisfactory. Ueda (1949) attempted a structure determination on the basis of visual estimation of intensities from powder patterns. None of the likely structures permitted by the space group yielded a satisfactory set of structure factors. Calculations were also made for arrangements of sulfur atoms alone. Curiously, it was found that a hexagonal close-packed arrangement gave structure factors in reasonable agreement with those observed. From this Ueda concluded that the copper atoms were in complete disorder.

The present paper describes a single-crystal investigation of the structure of high-chalcocite and discusses the probable relation of this structure to that of low-chalcocite. Refinement of the low-chalcocite structure is in progress and will be described in a subsequent paper.

EQUIPOINT RESTRICTIONS AND NATURE OF THE PATTERSON FUNCTION FOR HIGH-CHALCOCITE

The unit cell of high-chalcocite contains only 2 Cu_2S. This requires that ordered Cu and S atoms occupy special positions. Table 1 lists posible equipoints for the probable high-chalcocite space group $P6_3/mmc$. (It is interesting to note that examination of the other two possible space groups, $P3/m2c$ and $P6_3mc$, shows that the former has special positions identical with those listed, and that the latter has but two possibilities which are included in the list.) The S atoms may be accommodated in only one equipoint of rank 2. The Cu atoms may be accommodated in either two equipoints of rank 2, or a single equipoint of rank 4. A total of 20 arrangements of atoms in these equipoints is possible. Three possibilities, however, result in c being half that actually observed and may be discarded. Of the remaining arrangements, only 9 combinations are distinct.

TABLE I. SPECIAL POSITIONS LYING ON THE 6-FOLD AND 3-FOLD AXES IN SPACE GROUPS $P\,6_3/mmc$ AND $P3/m2c$

Equipoint	Coordinates in hexagonal cell		Corresponding coordinates in 2-dimensional representation	
2*a*	$0\ 0\ 0$	$0\ 0\ \frac{1}{2}$	$0\ 0$	$0\ \frac{1}{2}$
2*b*	$0\ 0\ 0$	$0\ 0\ \frac{3}{4}$	$0\ 0$	$0\ \frac{3}{4}$
2*c*	$\frac{1}{3}\ \frac{2}{3}\ \frac{1}{4}$	$\frac{2}{3}\ \frac{1}{3}\ \frac{3}{4}$	$\frac{2}{3}\ \frac{1}{4}$	$\frac{1}{3}\ \frac{3}{4}$
2*d*	$\frac{1}{3}\ \frac{2}{3}\ \frac{3}{4}$	$\frac{2}{3}\ \frac{1}{3}\ \frac{1}{4}$	$\frac{2}{3}\ \frac{3}{4}$	$\frac{1}{3}\ \frac{1}{4}$
4*e*	$0\ 0\ z$ $0\ 0\ \frac{1}{2}+z$	$0\ 0\ \bar{z}$ $0\ 0\ \frac{1}{2}-z$	$0\ z$ $0\ \frac{1}{2}+z$	$0\ \bar{z}$ $0\ \frac{1}{2}-z$
4*f*	$\frac{1}{3}\ \frac{2}{3}\ z$ $\frac{2}{3}\ \frac{1}{3}\ \frac{1}{2}+z$	$\frac{2}{3}\ \frac{1}{3}\ \bar{z}$ $\frac{1}{3}\ \frac{2}{3}\ \frac{1}{2}-z$	$\frac{2}{3}\ z$ $\frac{1}{3}\ \frac{1}{2}+z$	$\frac{1}{3}\ \bar{z}$ $\frac{2}{3}\ \frac{1}{2}-z$

Solution of a three-dimensional Patterson function involving atoms in these equipoints may be considerably simplified by noting that these special positions lie on the 3-fold and 6-fold axes in the hexagonal cell. These axes all lie on a (110) plane through the hexagonal cell. Fig. 1 shows that this plane is equivalent to the section ($0yz$) in the orthohexagonal cell. Analysis of three-dimensional Patterson maps is therefore reduced to a two-dimensional problem, since only this special section need be considered. Equipoint coordinates in this section are also given in Table 1.

INVESTIGATION OF THE LOW-CHALCOCITE STRUCTURE

An attempt was at first made to determine the crystal structure of low-chalcocite directly. A small fragment of Bristol, Connecticut, chalcocite was used in collecting a three-dimensional set of intensities. Using an equi-inclination Geiger-counter diffractometer, all of the accessible independent reflections in a MoKα sphere were investigated. The superstructure reflections were generally quite weak and a large number were not detectable. A total of 584 independent intensities were collected. Of these 76, or roughly 13%, were substructure reflections. Appropriate corrections were made for Lorentz and polarization factors. Absorption effects were not too serious and corrections were not made at this stage of the analysis.

A set of three-dimensional Patterson maps were synthesized. As might be expected, these were completely dominated by the marked substructure and

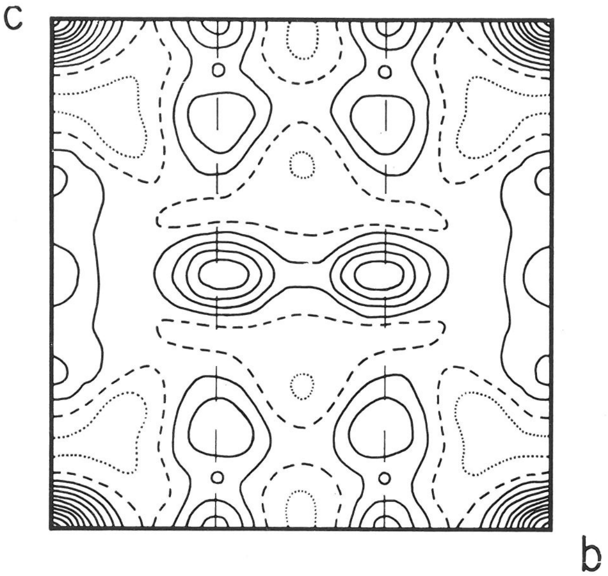

FIG. 2. Low-chalcocite substructure Patterson section $P(0yz)$. The lines $\frac{1}{3}z$ and $\frac{2}{3}z$ correspond to the location of the 3-fold axes in high-chalcocite. Contours at equal but arbitrary intervals. Negative contours dotted, zero contour dashed, positive contours solid lines.

proved to be uninterpretable. It was then hoped that analysis of the substructure alone might indicate the structure of high-chalcocite and yield some clue to the nature of the distortions responsible for the low-chalcocite superstructure.

Accordingly, three-dimensional Patterson maps were synthesized using only squares of structure factors obtained from the substructure reflections. These data had marked pseudo-hexagonal symmetry. The departures from this symmetry were significant enough, however, to warrant treatment of the data as orthorhombic. It was found that all peaks in the maps lay in the section $0yz$ of the orthorhombic cell. The coordinate y had only values of 0, $\frac{1}{3}$ or $\frac{2}{3}$. Therefore all electron density in the substructure is located at positions corresponding to special positions on the 3-fold and 6-fold axes in the hexagonal high-chalcocite cell.

The problem could then be treated as a two-dimensional one, as outlined in the preceding section. The Patterson section $P(0yz)$ is given in Fig. 2. None of the nine possible high-chalcocite structures yield Patterson maps which compare favorably with this section. In fact, it is readily seen that this map contains contradictory features: the peaks having coordinates of roughly (0, .3) and ($\frac{1}{3}$, .2) would require Cu in the 4-fold position having a variable parameter z. On the other hand, the strong peak at ($\frac{1}{3}$, 0) requires Cu in a position having the same z parameter as S, that is, in a symmetry-fixed 2-fold position. This map therefore had no clear-cut interpretation and suggested that an appreciable amount of electron density of displaced atoms in the low-chalcocite structure contributes to the substructure. This made a direct determination of the high-chalcocite structure advisable.

INVESTIGATION OF THE HIGH-CHALCOCITE STRUCTURE

Selection of material. Well-crystallized chalcocite from Bristol, Connecticut, was also used for this investigation. An attempt was made to grind spheres from this material using an apparatus similar to that described by Bond (1951). It was found that irregular fragments rapidly assumed the form of oblate ellipsoids but, upon further grinding, became misshapen pellets. The specimen finally selected was untwinned and had the form of an oblate ellipsoid of revolution with dimensions .505×.505×.251 mm. ($\mu_l r_{\max}=6.26$, $\mu_l r_{\min}=3.11$ for MoKα radiation). It was felt that this regular shape, for which exact absorption corrections could be made, was to be preferred to an irregular pellet which would require a smaller but less exact correction. Also, the specimen must be held at an elevated temperature while the intensities are collected. Chalcocite gradually deteriorates when heated in air. The larger regular shape had the advantage of having a higher volume-to-surface ratio, which makes this effect less serious.

Collection of intensities. A photographic technique was used to record the intensities. All reflections on a given level were therefore equally affected by any slight deterioration of the crystal. The method also had the advantage of providing evidence that no superstructure reflections were present. This would have permitted detection of a drop in temperature had the heating unit malfunctioned during the course of collecting the intensities.

Intensities were recorded with the aid of an integrating precession camera. The crystal was maintained at 125°±5° C. by a small radiant heater similar to one described by Morimoto and England (1960). The unit cell dimensions determined are in good agreement with those determined by Buerger and Buerger (1944) and Djurle (1958) as shown in Table II.

A disadvantage of recording intensities by the precession method is that the blind region in the center of upper level films obscures certain reflections. This usually requires use of several settings of the spindle axis if all attainable reflections are to be recorded. Because high-chalcocite has high symmetry and a small unit cell, all independent reflections lay outside of the blind region. It was therefore possible to record all intensities with one setting of the spindle axis. Several exposure times were used to insure that the linearity range of the film was not exceeded.

All films were developed simultaneously. Intensities were determined with a Joyce-Loebl Company double-beam recording microdensitometer. A total of 106 reflections were measured. Of 37 independent reflections, 7 were undetectable and were assigned half the minimum observable value. Lorentz and polarization corrections were computed for each reflection of the pair which compose a spot on the film. Transmission factors for each reflection of the pair were determined using a program for the I.B.M. 7090 computer (Wuensch and Prewitt, 1962). These transmission factors were suitably combined with the individual Lorentz and polarization factors. After applying these corrections, the average deviation between equivalent F^2's was 9.5%.

Solution of the structure. A three-dimensional Patterson function was synthesized using the I.B.M. 7090 program ERFR2 (Sly, Shoemaker and Van den Hende, 1962, unpublished). The problem was again reduced to a two-dimensional problem by considering the ortho hexagonal section $P(0yz)$, Fig. 3. It may be noted that this map is similar to the corresponding low-chalcocite substructure Patterson section, Fig. 2, except that the contradictory peak at $\frac{1}{3}$, 0 has diminished. The maxima with variable parameter, z, however, are no longer discrete peaks, but are instead smeared out over a considerable region of the cell. Fig. 4, for example, gives the Patterson section $P(xy\frac{1}{6})$. The distribution of the maximum is practically uniform except for very slight peaks in three symmetric locations about the 3-fold axis. The copper atoms are therefore disordered. This suggests that the Cu atoms are disordered. As a result, none of the nine "ideal" structures considered in the previous section predicted Patterson functions in reasonable agreement with Fig. 3.

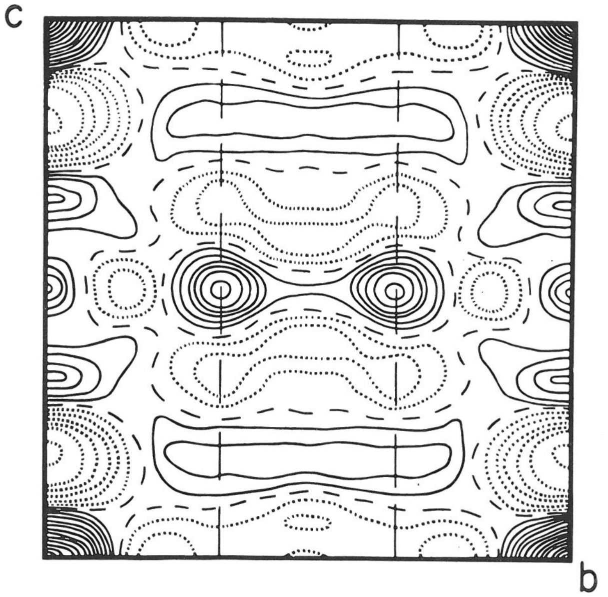

FIG. 3. High-chalcocite Patterson section $P(0yz)$ for the orthohexagonal cell. The lines $\frac{1}{3}z$ and $\frac{2}{3}z$ correspond to the location of the 3-fold axes. Countours at equal but arbitrary intervals. Negative contours dotted, zero contour dashed, positive contours solid lines.

The structure was solved with the aid of implication diagrams (Buerger, 1959) and successive electron density and difference maps. For structures containing a 6_3 axis of symmetry, the implication map $I_3(xy0)$ gives a projection of the structure along c with a 3-fold ambiguity (*i.e.*, the projected atoms are

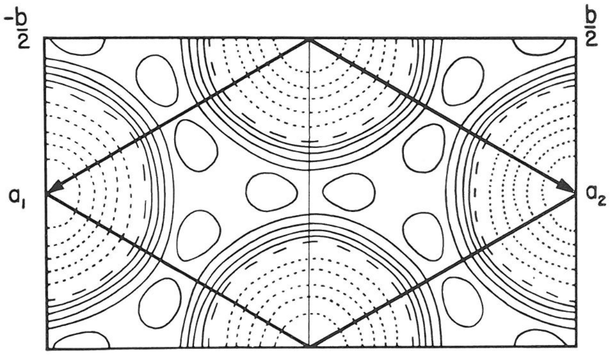

FIG. 4. High-chalcocite Patterson section $P(xy\frac{1}{6})$. Both the hexagonal cell and the orthohexagonal cell are indicated. Negative contours dotted, zero contour dashed, positive contours solid lines at half the interval of Fig. 3.

TABLE II. UNIT-CELL DIMENSIONS OF HIGH-CHALCOCITE

T	Buerger and Buerger (1944)	Present[1] study	Djurle (1958)		
	112°	1.25°	152°	300°	460°
c (Å)	6.68	6.75	6.722	6.761	6.806
a (Å)	3.89	3.95	3.961	3.981	4.005
c/a	1.717	1.710	1.697	1.698	1.699

[1] Precision .3%, accuracy about 1%.

produced about both the 6_3 axis and the two 3-fold axes of the cell). The implication map $I_6(xy\frac{1}{2})$ gives the structure without ambiguities, but with satellite peaks located at distances from the origin which are twice those of the atomic coordinates. These maps revealed that the main part of the electron density not confined to the 6_3 and 3-fold axes had x, y coordinates of 0, $\frac{1}{2}$. In space group $P6_3/mmc$ this is special position $6g(0\frac{1}{2}0)$.

Three-dimensional electron density maps were then synthesized using structure-factor signs based on hexagonal close-packed sulfur atoms and various fractions of Cu in equipoint $6g$. These maps all indicated positions $2b(00\frac{1}{4})$ and $4f(\frac{1}{3}\frac{2}{3}z)$, with $z\approx.6$ as additional sites of high Cu density. Further electron density and difference maps based on Cu atoms in one or two of these three suggested sites always returned the density in the remaining sites. This distribution of Cu was therefore taken as the correct approximation to the mobile Cu atoms. The final electron density maps showed electron density connecting the three Cu sites. The Cu atoms are therefore "smeared" as suggested above.

Refinement. Refinement was performed on the I.B.M. 7090 computer with the full-matrix least-squares program SFLSQ3 (Prewitt, 1962, unpublished). Only one scale factor was used. Reflections were initially assigned equal weights, but were weighted by $1/F_o$ in the final cycles.

In addition to the usual parameters, the weights of the three types of Cu atoms were also refined, subject to the restraint that the sum of the Cu atoms per unit cell be equal to 4. Following each series of cycles the distribution of weight was tested with electron density and difference maps. The Cu distribution given in Table III yielded a disagreement factor $R=\Sigma|\ |F_o|-|F_5|\ |/\Sigma|F_o|$ of 32% when the unobserved reflections were excluded. Observed and calculated structure factors are compared in Table IV. Investigation of the improvement of the agreement between F_c and F_o with variations in Cu distribution is being continued.

TABLE III. COORDINATES AND WEIGHTS OF ATOMS IN FINAL APPROXIMATION TO DISORDERED HIGH-CHALCOCITE STRUCTURE

Atom	Equipoint	Coordinates	Temperature factor
1 S	$2d$	$\frac{2}{3}$ $\frac{1}{3}$ $\frac{1}{4}$	.43
.870 Cu′	$2b$	0 0 $\frac{1}{4}$	.15
.355 C″	$4f$	$\frac{1}{3}$ $\frac{2}{3}$ .568	4.73
.140 Cu‴	$6g$	0 $\frac{1}{2}$ 0	3.28

TABLE IV. OBSERVED AND CALCULATED STRUCTURE FACTORS

hkl	F_o	F_c
00·4	11.56	11.94
00·6	9.86	−10.02
00·8	3.24	2.42
10·1	2.06	2.26
10·2	10.81	− 8.85
10·3	14.95	− 7.41
10·4	2.68	4.80
10·5	2.05	1.24
10·6	0.99[1]	− 1.69
10.7	3.40	− 2.31
20·0	2.93	4.57
20·1	5.11	− 2.07
20·2	5.12	− 5.01
20·3	5.11	5.42
20·4	6.73	4.77
20·5	1.87	− 1.92
20·6	7.40	1.31
30·0	6.06	10.63
30·1	0.83[1]	0.00
30·2	6.37	− 6.41
30·3	1.89	0.00
30·4	3.67	2.76
11·0	5.60	16.26
11·2	8.48	− 9.12
11·4	6.83	9.02
11·6	6.01	− 2.92
21·0	4.01	2.96
21·1	3.02	2.10
21·2	1.79	− 5.06
21·3	3.33	− 4.23
21·4	0.84[1]	0.04
21·5	1.09[1]	− 2.32
21·6	1.00[1]	1.21
31·0	1.88	− 1.31
31·1	2.60	− 2.33
31·2	1.26[1]	1.30
31·3	0.73[1]	− 2.17

[1] One-half minimum observable value.

DISCUSSION OF THE STRUCTURE

The disordered high-chalcocite structure contains sulfur atoms in hexagonal close-packing and mobile Cu atoms statistically occupying 3 types of sites. Cu′ lies in the S layers forming a trigonal Cu-S sheet. Cu″ occupies the available tetrahedral sites. Covellite, CuS, also exhibits a curious combination of CuS layers and tetrahedrally coordinated Cu. The remaining Cu‴ atoms are located on three edges of the S tetrahedron and thus statistically link an S atom to three S atoms in the neighboring sheet. Two-fold coordination is found also in Cu_2O.

The Cu-S bond lengths are 2.28 and 2.06 Å for Cu′ and Cu‴ respectively. Cu″ is not located in the center of the S tetrahedron, but has three neighbors at 2.59 Å and one at 2.15 Å. With the exception of Cu‴-S, these distances are in reasonable agreement with values of 2.26 and 2.29 Å found in CuAgS (Frueh, 1955). The distance Cu′-Cu″ is 2.59 Å, in good agreement with the distance 2.556 Å found in metallic copper. Cu″ and Cu‴, however, are too close to be occupied simultaneously in an ordered structure.

It is of interest to compare the disordered high-chalcocite structure with that of stromeyerite (Frueh, 1955) which is illustrated in Fig. 5. The structure consists of alternate layers of hexagonal Cu-S rings and close-packed Ag sheets. The mineral is orthorhombic, but is markedly pseudohexagonal as illustrated by the bond angles indicated in the Cu-S and Ag layers. The Cu-S sheets are stacked in nearly hexagonal close-packing. The Ag layers, however, are displaced along *b* such that each Ag atom is coordinated by two S atoms in neighboring layers. The sheets are knit together by these zig-zag Ag-S chains.

The relative arrangement of the layers in stromeyerite is perhaps best illustrated by the arrangement of atoms lying in the section (0*yz*) of the unit cell. This section is compared with the corresponding section of the idealized high-chalcocite structure in Fig. 6. The unit-cell dimensions of the two structures are quite similar, with the exception of the *c* axis. This difference is in part due to the larger radius of the Ag atom.

It may be seen that the structures differ only in two respects. The Ag atom in stromeyerite links a S atom to only one S atom in the neighboring sheet, while the corresponding S in high-chalcocite is statistically linked to all three neighboring S. Secondly, some of the Cu has escaped into the tetrahedral sites. Consequently, stromeyerite may be considered a derivative structure of the disordered high-chalcocite structure, formed by ordering the linkage between Cu-S sheets and by relegating the remaining tetrahedral Cu to the Cu-S sheet.

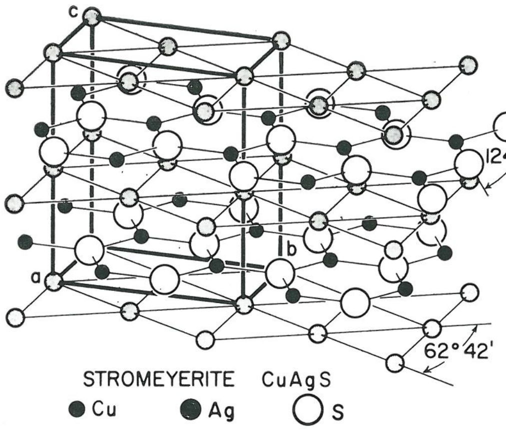

FIG. 5. The crystal structure of stromeyerite, CuAgS.

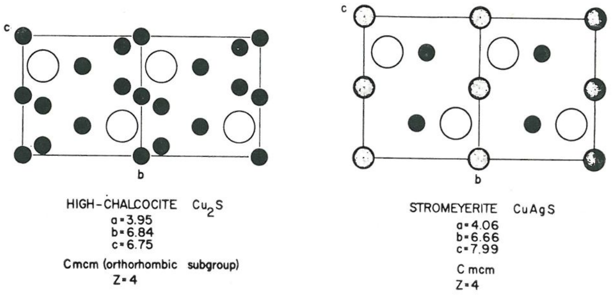

FIG. 6. Comparison of crystallographic data and electron density sections 0*yz* for the disordered high-chalcocite structure and stromeyerite.

At 93° C stromeyerite undergoes a phase transformation to a hexagonal modification (Djurle, 1958*b*), in striking similarity to the transformation in low-chalcocite at 110° C. The structures therefore have similar thermal properties and it seems very likely that the structure of high-stromeyerite may involve disorder of the type found for high-chalcocite. Furthermore, this may be the nature of the displacements relating high- and low-chalcocite. As mentioned above, the low-chalcocite substructure Patterson maps indicate a larger fraction of Cu occupying the Cu-S sheets. The relation between stromeyerite and high-chalcocite is compatible with such a displacement. Refinement of a model structure for low-chalcocite based on a suitable stromeyerite-like arrangement of atoms is in progress and will be described in a subsequent paper.

ACKNOWLEDGEMENTS

The authors are indebted to Dr. J. T. England of the Geophysical Laboratory for the design of the precession camera heating unit, and to Professor Alexander Rich of the Department of Biology, M.I.T., for the use of his laboratory's densitometer. All computations were performed on the I.B.M. 7090 computer at the M.I.T. Computation Center. This work was supported by a grant from the National Science Foundation.

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DISCUSSION

N. MORIMOTO (Tokyo): 1. How do you deal with the moving Cu atoms in the structure in order to calculate structure factors?

2. What is the most important difference between your structure and Belov's structure?

AUTHOR'S REPLY: 1. Inasmuch as the Cu atoms are somewhat "smeared," there is no really satisfactory way of treating this problem. The best approximation used was to split the Cu atoms into fractional parts. Even this treatment, however, assumes atoms distributed statistically in an equipoint of higher rank and not a continuous "cloud."

2. Belov and Butuzov proposed an ordered, symmetry-fixed structure with 2S in *2c*, 2Cu in *2b* and 2Cu in *2d*. The structure consists of S atoms in hexagonal close-packing. The Cu atoms occupy all the triangular interstices in the S layers.

P. R. BRETT (Washington, D. C.): Have the authors analyzed the chalcocite with which they worked? *X*-ray diffractometer studies at the Geophysical Laboratory on synthetic chalcocite show that both the position and intensity of reflections can change markedly by a variation in the sulfur content of the chalcocite as little as 0.1 wt. per cent. It is impossible to analyze natural chalcocite to this degree of accuracy.

AUTHORS' REPLY: We have not analyzed the specimens used, but analyses reported for Bristol, Conn. chalcocite show nearly ideal stoichiometry. Posnjak, Allen and Merwin,[1] for example, report Cu:S = 2.007:1.

An excess of 0.1 wt. per cent S would correspond to a composition of approximately $Cu_{1.99}S$. A variation of 0.4 wt. per cent, however, would result in Djurle's (1958*a*) new phase $Cu_{1.96}S$. The powder pattern of this phase is quite similar to low-chalcocite. This phase, however, inverts to a cubic digenite-like structure at 100° C. Since the hexagonal high-chalcocite structure was actually observed, Djurle's work would require any S excess to be less than 0.4 wt. per cent at most.

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[1] *Econ. Geol.* **10,** 508 (1915).