National Bureau of Standards Special Publication 364, Solid State Chemistry, Proceedings of 5th Materials Research Symposium, issued July 1972.

PHASE CHANGES IN CU_2S AS A FUNCTION OF TEMPERATURE

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The high-copper phase boundary of Cu_2S deviates from stoichiometry above 300 °C, first becoming copper deficient, then above ~ 1075 °C becoming copper rich. The maximum copper content occurs at the monotectic temperature of 1104 °C. The strong effect of oxygen on the hexagonal-cubic transition in Cu_2S was confirmed; the transition was also found to be sensitive to the type of pretreatment of the material. The high temperature tetragonal "$Cu_{1.96}S$" phase is stable between $Cu_{1.95}S$ and Cu_2S, at temperatures of ~ 90° to ~ 140 °C. The transition to the tetragonal phase is extremely sluggish. The true composition of djurleite has been shown to be approximately $Cu_{1.93}S$.

The phases near the chalcocite-digenite region of the diagram may be grouped into those with hexagonal close packing of sulfur atoms and those with cubic close packing of sulfurs. This is important in understanding rates of transformation among the various phases that occur in this area of the diagram.

Key words: Chalcocite; Cu_2S; digenite; djurleite; nonstoichiometry; phase relations.

1. PREVIOUS WORK

Fairly thorough explorations of the Cu-S phase diagram between Cu_2S and $Cu_{1.7}S$ have been made by a number of previous workers [1-8][1]. The resulting diagram may be seen in figure 1 taken largely from Roseboom [7] and Rau [8]. The principal phases are chalcocite (Cu_2S), orthorhombic (or monoclinic [9]) below 103.5° and hexagonal above it; djurleite (~ $Cu_{1.96}S$)[2], and digenite ($Cu_{2-x}S$), cubic with a wide range of solid solution at high temperatures, pseudocubic rhombohedral below 78° with a narrow range of solid solution. Additional phases which have been reported but which have not been confirmed as stable phases in the diagram are a tetragonal "$Cu_{1.96}S$," obtained between ~ 100° and ~ 150° [10-12], hexagonal $Cu_{1.91}S$, obtained by only one group [13], a hexagonal [14] polymorph of digenite [15], and a new "stable" ordering of digenite, known as anilite [16,17].

Several studies have examined the changing stoichiometry of chalcocite. Posnjak et al. [1] and Jensen [3] found the maximum melting point to be at a composition slightly deficient in copper. Rau [8] found approximately a linear relation for the maximum copper composition of chalcocite between $Cu_{1.9988}S$ at 516° and $Cu_{1.9939}S$ at 1048°. Wagner and Wagner [18] obtained a limiting composition of $Cu_{1.9996 \pm .0002}S$ at 400°. Wehefritz [19] obtained a formula of ~ $Cu_{1.998}S$ at 443° (cubic phase) but found no detectable deviation from stoichiometry in the hexagonal phase (*i.e.* copper content > $Cu_{1.9998}S$).

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] All chemical formulas will be given as the number of atoms of copper per atom of sulfur. All temperatures are °C.

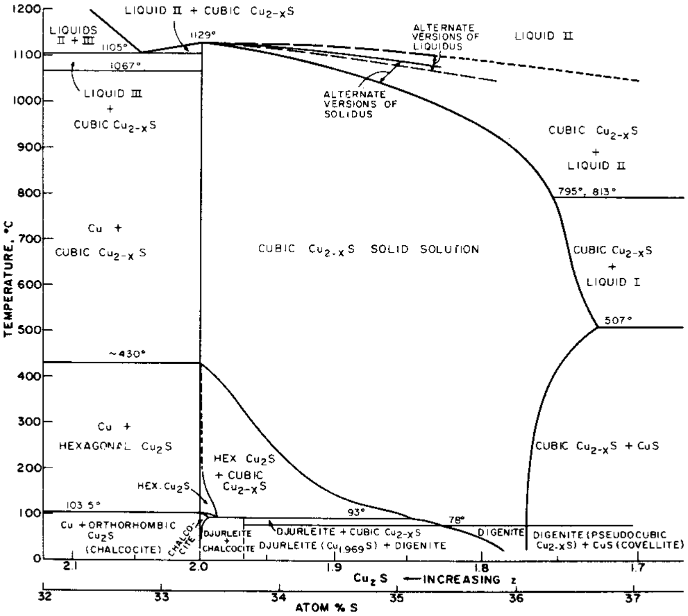

Fig. 1. Cu-S phase diagram in the vicinity of chalcocite and digenite [3, 6-8].

Much of the previous work, particularly near room temperature, was done in air on the assumption that little if any reaction with air occurs. Buerger [2] pointed out that this assumption was not valid, but his work was later criticized [5] because much of it had been done in air. Studies on chalcocite crystals chemically converted from CdS [14] re-emphasized that it was necessary to completely exclude air at all temperatures if the objective was to determine the two component diagram. The only one to have done so is Jensen [3], and our results are in agreement with his.

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

Raw materials were 99.999% Cu in either rod or 1 mm wire form and 99.999% S, both from American Smelting and Refining Co. The major impurity in the sulfur is organic material. The copper was etched in 1:2 or 1:3 HNO_3 to remove the oxide and superficial impurities, washed with distilled water, and kept in vacuum until use. Copper filings were not used because of the increased amount of oxygen impurity that would be present due to the large surface area. The sulfur was kept in vacuum briefly before use also in order to remove as much adsorbed oxygen and H_2O as possible. Only chunk sulfur was used so that none would be lost. Compositions were recalculated after weighing and applying the buoyancy correction to give the exact composition of the mix. From the time they were made, all compositions were kept sealed in vacuum except when being ground of x-rayed.

For the usual mixes, which ranged between 1 and 2-1/2 grams, compositional uncertainty was 0.05 to 0.1% in the Cu:S ratio, $Cu_{1.9599 \pm 0019}S$, for example. For the "whisker" compositions, which were weighed on a semi-microbalance, the estimated precision of the final compositions was ~ 2 to 4 ppm, equivalent to a formula of $Cu_{2.001151 \pm .000005}S$, for example. At this inaccuracy level, impurities can constitute an error up to ten times the weighing error. However, it is here assumed that due to the similar nominal level of impurities in the two raw materials, no substantial increase in error existed. If this is incorrect, it could shift the abscissa laterally in figure 3 by a small amount.

This work used mainly three techniques: observation of changes at high temperature (Cu "whisker" growth of Cu_2S samples), differential thermal analysis (DTA), and low temperature equilibrium at several temperatures, particularly 120° ± 1°, 73° ± 0.4°, and room temperature (24° ± 2°). Powder x-ray diffraction patterns were taken on most of the samples using film or a diffractometer.

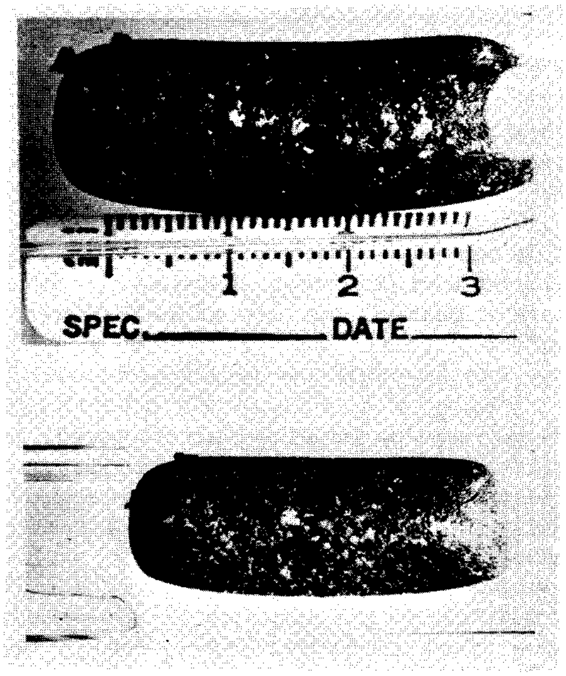

Fig. 2. $Cu_{2.00115}S$ composition showing the effect of heating to 608° for 1.3 hours. The upper picture (with cm scale) shows sample after equilibration at 100° (no whiskers). The lower picture shows the presence of numerous fine copper whiskers, particularly along the bottom edge of the sample.

After reaction (generally at 600° for 16 hours to several days, followed by slow cooling over several more days to allow re-equilibration), most samples were ground, divided into several parts, and resealed in fused silica. One part was used for the DTA (Dupont 900 unit with 1600° furnace); other parts were held at 120°, 73°, and room temperature. Where an appreciable vapor pressure was expected, the vapor space was reduced to a minimum by inserting a hollow slug before sealing. The DTA equipment was calibrated against the melting point of tin (231.89°) [20], cadmium (320.9°) [20], zinc (419.505°) [21], silver (960.8°) [20], and gold (1064.5°) [22], both at the beginning and near the end of the work. The temperature correction was never more than 3°. Temperatures normally reproduced to better than 1°.

The determination of the copper-rich Cu_2S phase boundary rests on an observation by Shiozawa [23]. If a Cu_2S sample has been saturated with copper at a low temperature and is heated somewhat hotter, very fine copper whiskers will grow out of the surface of the Cu_2S, indicating it is now supersaturated and is in the two-phase Cu-Cu_2S region of the diagram. When the sample is cooled the whiskers redissolve in the Cu_2S. Since very small amounts of free copper can be detected visually, this is therefore a very sensitive means of plotting this phase boundary. An example showing the same sample with and without the copper whiskers is seen in figure 2.

The large samples to be used for the copper-saturated Cu_2S phase boundary were not ground after reaction, but were used as is. It is believed that the slow cooling permitted equilibration as low as 150°. The reaction progressed by copper migrating through the already-formed copper sulfide to the surface, where it reacted with sulfur vapor. This resulted in a hollow core at the completion of the reaction of almost the size of the original copper rod. Any free copper remaining after the reaction was completed remained as a solid lump in the hollow core.

A thermocouple (calibrated against a NBS standardized reference thermocouple) was fastened to the outside of the container with the bead aligned with the middle of the Cu_2S piece, and the assembly was put in a temperature-stabilized furnace for a length of time necessary to establish equilibrium. For low temperatures, > 16 hours was used, while near 1000° times of 15 minutes to 1/2 hour were sufficient. The length of the samples meant that at high temperatures a small temperature gradient ($< 5°$) existed within the sample. The magnitude of the gradient was estimated with the thermocouple, and corrected for.

After heating, the sample was very quickly removed from the furnace and examined for the presence of copper whiskers. Most of the time, samples not showing copper whiskers were heated in order to see if whiskers appeared, but occasionally the reverse procedure was used: samples in which whiskers had been formed were heated at a different temperature to see if the whiskers disappeared. As far as could be determined, both methods gave the same results.

Two observations should be made on problems encountered, in case others should wish to repeat the experiments. Whiskers that formed quickly at low temperatures tended to redissolve quickly, but if they remained for 16 hours, extensive treatment (usually at very high temperature) was necessary in order to get rid of them. Thus for the tests involving disappearance of copper whiskers, the whiskers had to be "fresh". Also at high temperatures, the presence of a very small sulfur (or copper sulfide) vapor pressure resulted in whiskers converting to Cu_2S on the surface after a few hours, after which it was virtually impossible to get rid of them and the sample would have to be abandoned (since one is depending on visual appearance of whiskers). This caused premature abandonment of one of the compositions used in this study, that at about $Cu_{2.00115}S$.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The results of the present work and the previous literature are summarized in figures 3 - 5. The values of Rau [8], Roseboom [7], Ruhl and Sauer [24] and Wehefritz [19] have been accepted for the copper-deficient phase boundary of digenite ($Cu_{2-x}S$) between 130° and 1000°.

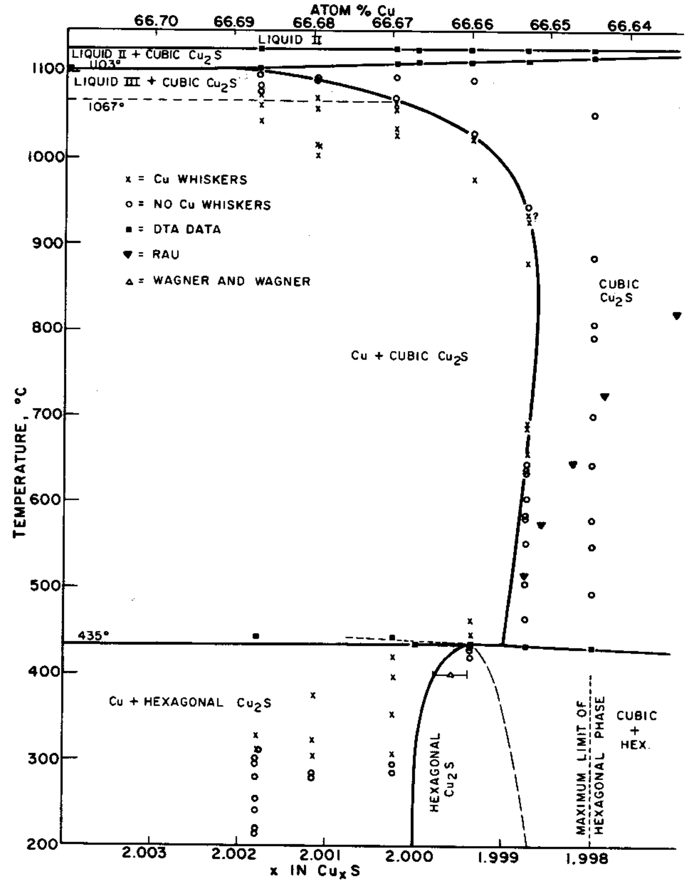

Fig. 3. The phase boundary between Cu_2S and $Cu_2S + Cu$.

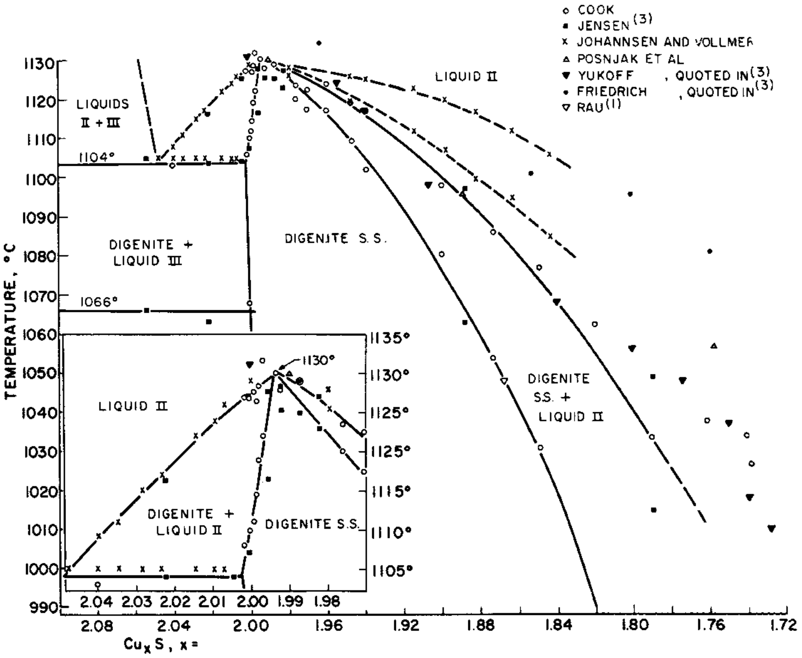

Fig. 4. Melting relations from $Cu_{2.1}S$ to $Cu_{1.72}S$. The previous literature is summarized along with results from the present study.

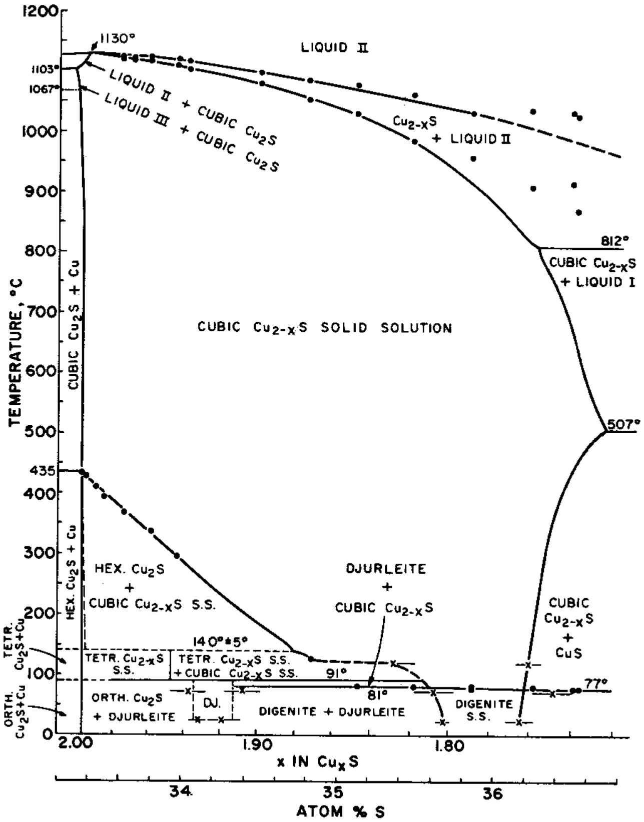

Fig. 5. Phase diagram from $Cu_{2.00}S$ to $Cu_{1.72}S$.

3.1. *Copper Solubility in Cu_2S and High Temperature Phase Relations*

The observation of Cu whiskers due to supersaturation with copper was used to determine the (Cu + Cu_2S) - Cu_2S phase boundary between 165° and 1070 °C, as shown in figure 3. At low temperatures, copper whiskers were most numerous at the hottest spot, which follows from the shape of the phase boundary (fig. 3). The copper whiskers varied in length up to half an inch or more. Long whiskers were usually bent or coiled. Widths of whiskers ranged from barely detectable under the microscope (< 10 microns) to several tenths of a millimeter. One whisker was found to be polycrystalline by x-ray diffraction. In at least some cases, the whiskers grew into the inner void as well as on the outside, but this did not appear to interfere with the observations. When the samples were broken open at the end of the experimentation, a very minor amount of whiskers was found in those samples with more than two copper atoms per sulfur, but no trace was found of the original copper core, indicating that at some stage all of the copper was in solid solution in the Cu_2S.

The initial deviation from stoichiometry is in the direction of copper deficiency as expected. However, as may be seen in figure 3 the boundary unexpectedly curves back towards copper at high temperature. This is in the opposite direction to what has been reported previously [8].

At low temperatures, all three samples with excess copper ($x > 2.0$) formed Cu whiskers on heating above ~ 305 °C. Since all were equilibrated with Cu near 150°, all showed whiskers at the same temperature, the excess copper at 150° remaining in the core as a solid piece. It must be only above 300° that the phase boundary deviates significantly from the stoichiometric composition. One sample was heated for long times near 305°, 320°, 400°, 415°, 435°, and 445° and the amount of free copper was qualitatively observed. At 304.5° no copper was detected. At 306° one exceedingly small whisker was found. At 320.5°, both the number and length of the copper whiskers had increased considerably, but the amount was still small. At 415° a further increase in amount of copper was observed. At 435° and at 445° the number of whiskers had probably not increased, but the thickness and length were both quite large. The longest whiskers were probably at least half an inch in length, and strongly coiled. These qualitative observations are the basis for the shape of the phase boundary below 435° as drawn in figure 3. It is assumed that copper-saturated compositions below 300° are stoichiometric, but the limits of uncertainty are $Cu_{2.0001}S$ and $Cu_{1.9999}S$ from compositions of samples adjacent to the phase boundary and observation of changes in amount of copper whiskers with temperature above 305°.

High temperature results were supplemented by data from the DTA curves, which showed the existence of solidus and liquidus curves on *both* sides of the maximum melting temperature of the Cu_2S phase as indicated in figures 3 and 5. The maximum melting point is in the composition range $Cu_{1.994}S$ to $Cu_{1.986}S$, probably at the high copper end of this range, and the maximum temperature of melting is 1130 ± 2°, in excellent agreement with 1130 ± 1° at $Cu_{1.990 \pm .004}S$ and 1129° at $Cu_{1.989}S$ reported previously [1,3]. It is probable that the occurrence of the maximum melting point slightly on the sulfur-rich side of Cu_2S led previous workers to suspect that the copper-rich phase boundary of the Cu_2S phase was shifted in the same direction at high temperatures [8,3], which is incorrect or oversimplified as seen above.

One notices in figure 3 that the "solid solution" of copper in Cu_2S at 1103° is appreciable. The data points from the "whisker" data just below 1095° indicating no formation of copper whiskers have been disregarded. The lack of apparent rise of the Cu-Cu_2S phase boundary is due to the circumstance that the specimens needed to be equilibrated at least 20° above the phase boundary for the whiskers to appear. The fact that the sample with composition $Cu_{2.001797}S$ was not supersaturated with copper at 1097° (the highest temperature to which it was heated) is shown by the absence of any core of unreacted copper when the piece was broken open.

The monotectic was measured at 1103 ± 2° for a composition with appreciable excess Cu (fig. 4) compared with 1105° determined previously [6,3]. Jensen [3] chose 1105° although his data contained both 1104° and 1105° as possible data points. The value of 1104° ± 1° is used for figure 1.

3.2. *The Hexagonal-Cubic Phase Transition Near 435°*

There has been a good deal of difficulty in determining the transition temperature in the past due to its sluggish nature, with temperatures between 350° and 470° reported; in this study it was *not* a problem, largely because of the rigorous efforts to exclude oxygen from the samples. The strong effect of oxygen on the phase transition was pointed out by Roseboom [7]. The minimum temperature hysteresis for the transition was 7°, considerably under most other studies, but still of significant size. Wehefritz [19] explained this large hysteresis as due to the extremely small heat of transition, estimated by him as 110 ± 40 cal/mole. This can be expected to be not far in magnitude from enthalpies due to structural defects and therefore arising from other than thermodynamic equilibrium.

An additional effect on the hysteresis was found arising from the past thermal history of the sample. All samples in which the composition contained more copper than the stable limit near 435° showed increased hysteresis with temperature cycling, even when oxygen was excluded, the increase in hysteresis amounting to a factor of three after several cycles. The effect was temporary, since re-equilibrating the sample at high temperature sharpened the DTA peaks and eliminated the excess hysteresis. The transition temperature was unchanged between samples equilibrated at 1105° (near maximum Cu content) and at 835° (near minimum Cu content). Thus the increased temperature hysteresis is caused by slow kinetics, probably caused by lattice defects connected with the Cu precipitation, rather than a shift of transition temperature with copper content.

There appears also to be a continued rise of the hexagonal-cubic phase transition as a metastable extension of the phase boundary into the two phase region (dotted in on figure 3) but the increase in temperature is small and is barely significant.

The shape of the DTA curves for the hexagonal-cubic transition in compositions near Cu_2S can also suggest a location for the minimum copper content of the hexagonal phase since a single phase sample will transform more sharply than a sample which is a mixture of the limiting hexagonal composition plus a cubic phase. From the curve shapes the limiting low copper content of the hexagonal phase is no lower than $Cu_{1.998}S$, and may be as high as $Cu_{1.9994}S$. This uncertainty is indicated on figure 3 by dashed lines. Roseboom [7] by a different method judged that the solid solution limit of hexagonal chalcocite at 180° was at higher copper content than $Cu_{1.998}S$, which is in agreement.

3.3. *Low Temperature Phase Relations*

A brief summary is given of other findings, since they affect the structural interpretation of the results.

No evidence was found for solid solution in "orthorhombic" chalcocite at 73° or 76° by the method of disappearing phases. No evidence near 100° (where solid solution was reported to be maximum [7]) could be obtained, since samples transformed to the tetragonal phase. By the same method the composition of djurleite was found to be $Cu_{1.93 \pm .01_5}S$. Results were not precise enough to be certain of the existence of solid solution. It is probable that previous studies used material that was slightly contaminated with oxygen, and thus contained less Cu in the lattice than was believed to be the case. Djurleite decomposes at 91 ± 1°, in reasonable agreement with the previously determined [7] 93°.

The transformation to tetragonal "$Cu_{1.96}S$" is very sluggish, and may again become more so in the presence of oxygen contamination. All compositions between $Cu_{2.00}S$ and $Cu_{1.95}S$ transformed completely to the tetragonal phase in a matter of months between the temperatures of 94° and 120°, and partially transferred at 137°. The phase transforms back by at least 146°. Lesser times were frequently insufficient for complete conversion.

$Cu_{1.91}S$ [13], the hexagonal polymorph of digenite [14,15], and anilite [16,17] were not obtained as stable phases in this study, and are not believed to exist in the equilibrium Cu-S phase diagram. The details of the attempts to obtain anilite will be reported elsewhere.

4. COMPARISON OF THE STRUCTURE OF THE COPPER SULFIDES

X-ray diffraction on small CdS crystals which had been chemically converted to chalcocite, djurleite, or "hexagonal digenite" demonstrate a great similarity in the structure [14], which can be explained by assuming that the sulfur atoms remain fixed while the copper atoms, which are known to be unusually mobile in Cu_2S [4, 25], rearrange themselves in accordance with the proportion of copper atoms to sulfur. Chalcocite, both hexagonal [26] and "orthorhombic" [9,26] forms, has its sulfurs essentially in hexagonal close packing. Psuedo-hexagonal [27] djurleite and the hexagonal polymorph of digenite are both obtainable from chalcocite as *single* crystals [14], indicating the same sulfur arrangement. Eliseev's [13] $Cu_{1.91}S$ phase can also be fitted to this sulfur arrangement (fig. 6).

The cubic close packed sulfur arrangement typified by sphalerite and hawleyite (cubic CdS) is found in digenite [28] (or anilite [16,17]) and tetragonal "$Cu_{1.96}S$" [10]. This is the obvious explanation for the very sluggish transition between "$Cu_{1.96}S$" and djurleite or chalcocite, and the somewhat sluggish transition between hexagonal chalcocite and digenite at 435°. On the other hand, while the cubic high temperature form of digenite can be at least partially quenched, the phase transformation to the low temperature ordered phase is sufficiently fast that the DTA peak occurs with no hysteresis. The hexagonal form for chalcocite is widely reported as unquenchable; the hexagonal-orthorhombic transition, though almost certainly first order and showing 10 to 15° hysteresis, occurs rapidly.

All of the above results are completely consistent with the picture of the two basic sulfur arrangements with the interstices filled by highly mobile copper atoms. Transitions between phases with the same sulfur arrangements are rapid while transitions between phases with different sulfur arrangements are sluggish. This same approach to phase relation among the copper sulfides has been clearly expressed in a recent paper by Cavallotti and Salvago [15]. It is obvious that the copper atoms, being highly mobile and able to take a wide variety of orderings, are very poorly bonded to the sulfur atoms. In fact a statistical distribution of copper atoms along channels has been proposed [26] for the structure of hexagonal chalcocite.

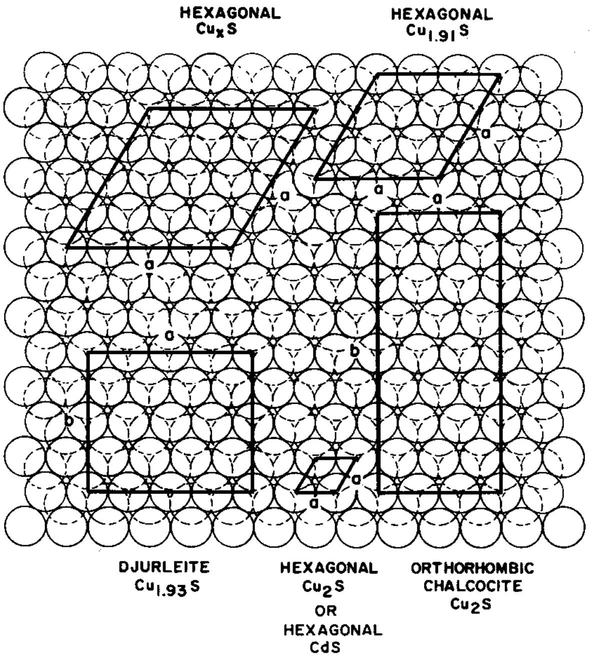

Fig. 6. Idealized unit cells in the plane perpendicular to *c* for copper sulfides, showing orientation and size of unit cells with respect to hexagonal close packed sulfur layers.

An additional problem is the reason for the wide solid solution in the structures with a cubic close packed sulfur arrangement and very limited solid solution in those with hexagonal close packed sulfurs. Cavallotti and Salvago [15] offered the following structural explanation. In the cubic type the coppers tend to be in the tetrahedral antifluorite position, whereas in the hexagonal close packed structures the coppers tend to be in the sulfur layer and are thus more tightly bonded to three sulfurs than when they are bonded to four in the cubic arrangements. This favors the cubic sulfur arrangement when the ratio of copper to sulfur deviates from 2:1.

5. ACKNOWLEDGMENTS

This work was performed while a Ph.D. candidate at Case Western Reserve University, and was supported in part by Aerospace Research Laboratories, Air Force Systems Command, United States Air Force, Contract F33615-68-C-1732. I am indebted to P. O. Banks and J. Hower of the Geology Department, Case Western Reserve University and L. R. Shiozawa and J. M. Jost of Gould Inc. for many stimulating discussions.

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DISCUSSION

H. T. Evans: In connection with your testimony that most natural chalcocite specimens actually are djurleite, I may say that from my own experience I can confirm this observation. However, I do not agree that the djurleites are psendomorphous after original low chalcocite. The specimen labelling is not important because djurleite closely resembles low chalcocite in physical properties, and djurleite was not known to be a distinct species before 1958. I have found that each has distinct and characteristic crystal habit, and from this evidence it appears that both have been formed as primary phases in the veins at temperatures below 100 °C. The djurleite crystals are flat, roughly hexagonal tablets, fresh in appearance, with blue-black submetallic luster. Low chalcocite crystals are more prismatic with dome terminations, highly striated, and have a dark, reddish brown-black patina resulting from surface oxidation. X-ray diagrams show that low chalcocite crystals are often intergrown with djurleite. Allowing for low temperatures of formation that are quite feasible in vein deposits, these observations are consistent with the equilibrium system you have shown.

W. R. Cook: In all cases but one, the crystals examined were old (mined over 43 years ago), and were almost entirely djurleite. One larger crystal that had been attached to copper sulfide matrix was still partly chalcocite, and one crystal which was unattached had gone all the way to digenite. However, all but one of these crystals (including the digenite) had shapes explicitly or implicitly hexagonal. Some were flat hexagonal plates, some were hexagonal prisms. The crystal retaining a little chalcocite was prismatic.

Basically, I have trouble visuallizing djurleite being as hexagonal in appearance as chalcocite, which *is* hexagonal above 103 °C. Therefore, I believe that all of these crystals were hexagonal to start with, and were chalcocite. The one crystal that was different was the Bristol Conn. specimen, which had the shape shown for it in Dana. The long axis of the crystal was the djurleite *a* axis. This crystal obviously grew below the stability range of the hexagonal form, and therefore could have been either low chalcocite or djurleite. My preference is for djurleite, because the composition is "different" and so is the crystal shape, but it is purely intuitive, and may be entirely incorrect.