

AN X-RAY INVESTIGATION OF SOME LOW-TEMPERATURE
SOLID PHASES OF THE SYSTEMS: $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$,
 $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$, $\text{Cu}_2\text{S}-\text{FeS}$, and $\text{Cu}_2\text{S}-\text{CuS}$.

by

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ABSTRACT

The x-ray investigations of the solid phases of the systems $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$ and $\text{Cu}_2\text{S}-\text{FeS}$ were undertaken on the premise that at low temperatures extensive solid solutions would be formed, as in the case of the system $\text{Cu}_2\text{S}-\text{CuS}$.

The methods used to synthesize the various intermediate phases were adopted and modified from previous work on the system $\text{Cu}_2\text{S}-\text{CuS}$ that was undertaken by Posnjak, Allen and Merwin and later by Newton W. Buerger. The experimental procedure consisted in taking x-ray powder photographs at elevated temperatures of previously annealed compacts which were made from mixtures of the pure sulfides.

The results of the investigations of the four systems studied were found to be of comparable accord with regard to the formation of cupro-, stibio-, arseno-, and ferro-chalcocite solid solutions; cupro-, stibio-, arseno-, and ferro-digenite solid solutions; and other analogous solid solutions which have been designated as the α -digenite series. Basic structural similarities of these phases were evident from the x-ray photographs. According to Rahlfs, digenite has an anti-fluorite structure in which some of the copper atoms are statistically distributed over many different sites; most probably in thermal disorder. The digenite structure has apparently been derived from that of high-temperature chalcocite, which has an hexagonal basic structure with complete interstitial disorder of the copper atoms. The members of the α -digenite series, that are lowest in Cu_2S content, were found to be cubic with a face-centered cell that is twice as long as the cell of digenite. In this respect, α -ferrodigenite appears to be identical with high-temperature bornite. With increasingly greater Sb_2S_3 content, the α -stibiodigenite series were found to exhibit a sphalerite-type structure. In the system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, the high-temperature phases, tetrahedrite (stylotypite) and chalcostibite were derived from the low-temperature digenite phases.

The rates of intermediate phase formation in the systems studied were observed to be very rapid and to obey Tammann's parabolic rate rule for diffusion. The diffusion process is apparently dependent on the prevailing interstitial disorder of the copper atoms in chalcocite.

In terms of geological significance, the role of solid-state diffusion has been stressed with regard to the formation of sulfosalt and complex sulfide phases in ore bodies located at moderate to great depths as well as those which undergo thermal metamorphism.

Thesis Supervisor: Martin J. Buerger

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Various minerals that were used during the investigation were supplied from the Harvard Mineral Collection through the kindness of Professor Clifford Frondel. The samples of chalcocite which were used throughout the course of study, were obtained through the courtesy of Alfred D. Wandke, formerly of the Department of Mining Geology at Harvard University.

The valuable comments and suggestions concerning diffusion, which were given by Professor Carl Wagner of the Department of Metallurgy, were deeply appreciated.

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PREFACE

The solid-state investigations of some of the low-temperature phases of the systems $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$ and $\text{Cu}_2\text{S}-\text{FeS}$ were originally pursued on the basis of the success of previous solid-state investigations of the system $\text{Cu}_2\text{S}-\text{CuS}$, that were made by Posnjak, Allen, and Merwin and later by Newton W. Buerger. A composite of phase data was eventually made for all four systems for comparison.

During the preliminary investigations, the intermediate phases encountered in these systems at low temperatures were found to be either isostructural or structurally related to the mineral digenite, Cu_9S_5 . As the study was systematized and intensified, the correct interpretation of the mechanism of formation of the intermediate phases was sought, since it was felt that this knowledge would have some bearing on the formation of the sulfosalt and complex sulfide minerals in ore deposits. Since solid-state syntheses depend on atomic diffusion, it was hoped that the actual degrees of sulfide "miscibility" encountered would provide useful data to assess the role of solid-state diffusion in such complex ore phenomena as "replacement".

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PREVIOUS WORK ON THE SYSTEM $\text{Cu}_2\text{S}-\text{CuS}$

The first inclusive study of the system $\text{Cu}_2\text{S}-\text{CuS}$ was made in 1915 by Posnjak, Allen, and Merwin (1), who indicated that there was a limited field of solid solution between chalcocite and covellite. The inversion temperatures of solid solutions of Cu_2S in CuS were recorded by using compacted mixtures of chalcocite and covellite which had been previously annealed at 110°C .

Bateman (2) in 1929, using natural crystals of chalcocite and covellite, discovered that within the temperature range of 75° to 150°C , as much as 30 to 40 percent covellite dissolved in chalcocite.

The most systematic investigation of the low temperature fields of the system $\text{Cu}_2\text{S}-\text{CuS}$ was carried out by Newton W. Buerger (3, 4) in 1939, by means of x-rays. Buerger succeeded in clarifying the pre-existing relationships between low-temperature and high-temperature chalcocite, and established the existence of the mineral phase digenite, Cu_9S_5 , which had been described as "isometric and blue chalcocite" on former occasions. Rahlfs (5) had assigned what is now known as the digenite phase an anti-fluorite structure in which some of the copper atoms were thought to be statistically distributed over many different sites. This phase was shown by Buerger to "dissolve" more CuS or Cu_2S at higher temperatures. An ordered phase having the "ideal composition", Cu_9S_5 , was considered to prevail below 47°C .

The method used by Buerger for developing the low temperature region of the phase diagram for the system $\text{Cu}_2\text{S}-\text{CuS}$ consisted essentially of homogenizing powdered mixtures of chalcocite from Bristol, Connecticut and synthetic covellite. The process involved pulverizing, compacting and annealing the material at 110°C for periods of 12 hours or longer.

On the basis of x-ray photographs taken on the homogenized material at elevated temperatures, Buerger described the existence of 3 compounds, 4 phases, and 7 phase fields within the system $\text{Cu}_2\text{S}-\text{CuS}$. The compounds were:

Chalcocite, "ideally" Cu_2S
 Digenite, "ideally" Cu_9S_5
 Covellite, CuS .

The phases were:

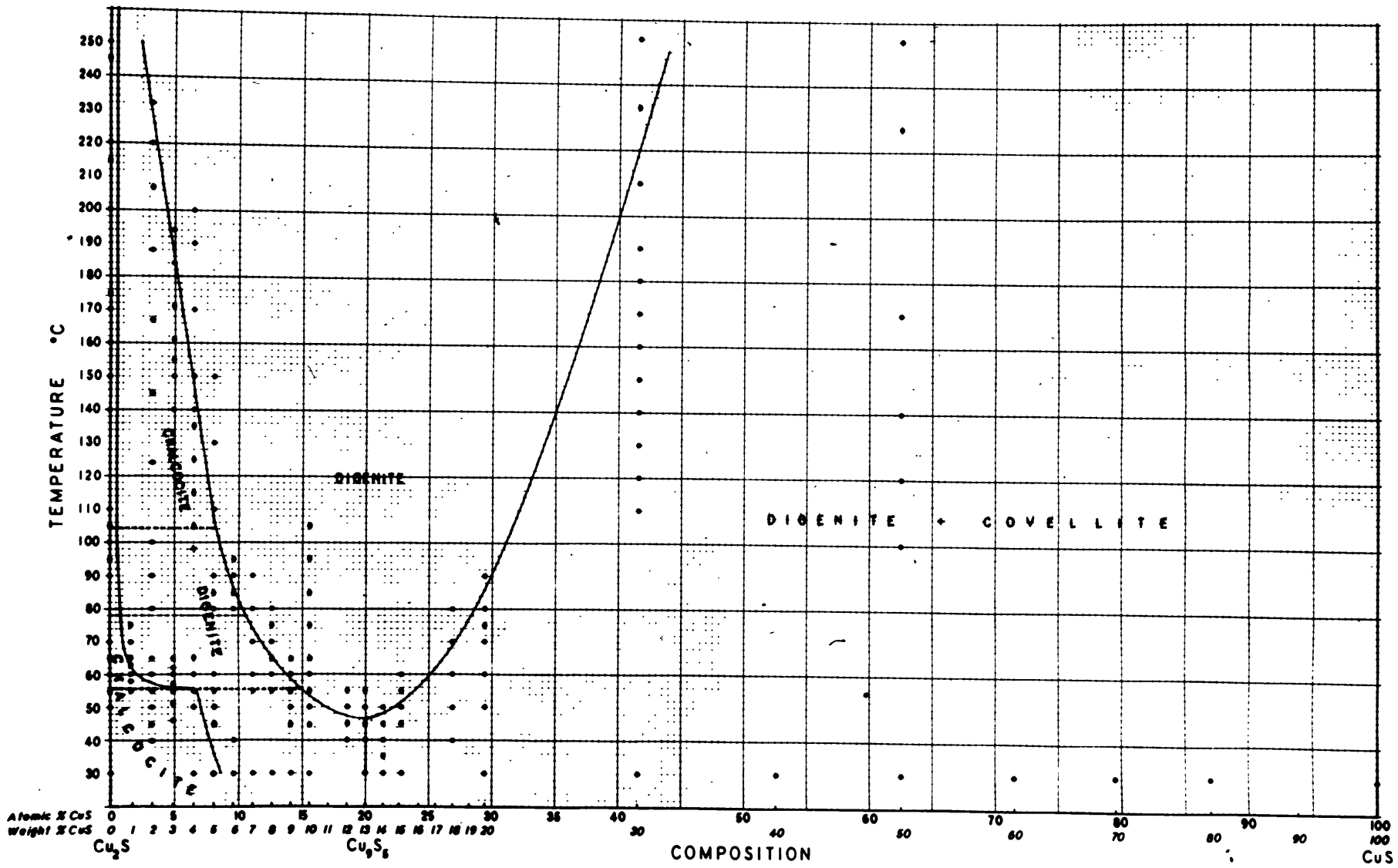
High-temperature, completely disordered chalcocite, which was shown by M.J. and Newton W. Buerger (6) to have an hexagonal basic structure in which the copper atoms are in complete interstitial disorder.
 Low-temperature chalcocite, orthorhombic superstructure.
 Digenite.
 Covellite.

The phase fields have been reproduced from the original work in Fig. 1.

During investigations leading to the origin of chalcocite, A.D. Wandke (7) of Harvard University had recourse to repeat and enlarge upon several aspects of the work performed by Newton W. Buerger. Wandke contended that if powdered mixtures of chalcocite and covellite had been annealed for longer periods of time than Buerger allowed, more

Figure 1

Diagram of the system $\text{Cu}_2\text{S}-\text{CuS}$, reproduced
from Newton W. Buerger (3).

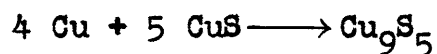
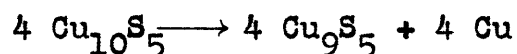


digenite would have been formed at the lower temperatures. Wandke also maintained that not all "blue" chalcocite is digenite since it has been found on x-ray examination to be structurally identical with anisotropic, white chalcocite.

To ascertain the mechanism by which digenite formed, Wandke devised a series of diffusion experiments. A cylinder, one-half centimeter in diameter, of pure, massive chalcocite from Keeweenaw, Michigan was embedded in natural covellite in a tube, which was evacuated, sealed, and maintained at 110°C for 96 hours. The cylinder was weighed before and after the run and was found to have undergone a loss in weight of about 7.7 percent, or theoretically, to have lost enough copper to have been altered to Cu_9S_5 . The procedure was reversed using instead a cylinder of covellite that was surrounded by powdered chalcocite. On completion of the run, the cylinder exhibited a swelled and cracked appearance and appeared to have been transformed into digenite. Further runs were made on blocks of chalcocite, and covellite, which were wired together and cut and polished across the interface to observe the minerals in contact. The blocks were placed in a pyrex tube that was evacuated, sealed and maintained at 115°C for 24 hours. Afterwards, on repolishing the specimen, Wandke noted that the covellite, up to 1.7 mm from the contact, had lost its anisotropism and had been transformed into digenite. The chalcocite block had widened its cleavage due to a loss of volume over the surface. By repeating the procedure for another 24 hours, the digenite

was found to have penetrated 3 mm deep into the covellite. Wandke described the front of attack as being "non-uniform" with the formation of "residuals of covellite like those in ores attributed to the replacement of covellite by digenite". X-ray photographs of the changed chalcocite and altered covellite indicated that both minerals had been transformed into digenite.

On the basis of these results, Wandke concluded that digenite was formed not only as a result of "the diffusion of copper ions out of chalcocite", but also by the "diffusion of copper ions into covellite". The equations given for the reactions were as follows:



whereby 4 mols of chalcocite were required to convert 1 mol of covellite to digenite.

PREVIOUS WORK ON THE SYSTEM Cu-Sb-S

As definite members belonging to the system Cu-Sb-S, there are listed in the currently revised edition of the Dana System of Mineralogy (8), the minerals:

Tetrahedrite,	$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$
Famatinite,	Cu_3SbS_4
Chalcostibite,	CuSbS_2

Styloptypite, a mineral having the composition, Cu_3SbS_3 , was

found in Copiapo, Chile by F. von Kobell and was later considered by Schneiderhöhn (9, 10) to be a specific variety of tetrahedrite. Falkenhaynite, a massive gray-black mineral from the Fiedler Vein, Joachimstal, Bohemia, having the same composition as stylumite, is described in the Dana System of Mineralogy (8) as "most probably an impure form of tetrahedrite".

Additional reports of compounds which were synthesized and which may be members of this system have appeared in the literature. Rammelsberg (11), reportedly synthesized the compound $3\text{Cu}_2\text{S} \cdot 2\text{Sb}_2\text{S}_3$ ($\text{Cu}_6\text{Sb}_4\text{S}_9$); the compound $\text{Cu}_2\text{S} \cdot 2\text{Sb}_2\text{S}_3$ ($\text{Cu}_2\text{Sb}_4\text{S}_7$) was produced by Sommerlad (12) along with chalcostibite and stylumite, by heating mixtures of CuCl and Sb_2S_3 . The first compound strongly resembled the mineral, guejarite, from Guejar, Spain. As a result of carrying out reduction decompositions of Sb_2S_3 intermixed with Cu_2S , Schenk, Hoffmann, Knepper, and Vogler (13) succeeded in combining the sulfides in the following proportions:

Cu_2S	:	Sb_2S_3	
1		1	2CuSbS_2
2		1	$\text{Cu}_4\text{Sb}_2\text{S}_5$
3		1	$2\text{Cu}_3\text{SbS}_3$
2		3	$\text{Cu}_4\text{Sb}_6\text{S}_{11}$
3		4	$\text{Cu}_6\text{Sb}_8\text{S}_{15}$
4		5	$\text{Cu}_8\text{Sb}_{10}\text{S}_{19}$
5		3	$2\text{Cu}_5\text{Sb}_3\text{S}_7$

The first extensive work on the equilibrium diagram of the system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ was performed in 1912 by Parravano and de Cesaris (14) who plotted isotherms for the various melts containing the sulfides. At 610°C , a eutectic mixture of Cu_2S and 18.4 percent of the compound Cu_3SbS_3 was formed; another eutectic mixture of Sb_2S_3 and 60.0 percent of the compound CuSbS_2 occurred at 490°C . The compound CuSbS_2 , which was described as chalcostibite, was observed to melt incongruently at 542°C to form Cu_3SbS_3 , which was thought to be analogous to stylotypite.

The pyrosyntheses that were carried out by Gaudin and Dicke (15) in 1939 in the system Cu-Sb-S verified the results of Parravano and de Cesaris, whose diagram constituted only a binary section of the larger ternary system. By the method of iridescent filming of the phases formed, the various compounds and solid solutions within the system were identified as tetrahedrite (including stylotypite), containing 23-26 molar percent sulfur, chalcostibite, containing 25.5-27.0 molar percent sulfur, and famatinite containing 28-31 molar percent sulfur.

Tetrahedrite was synthesized by R. Gaines (16) at Harvard University in 1951 hydrothermally at both low and high temperatures under pressure, and under both acid and alkaline conditions. Gaines also succeeded in precipitating famatinite at low temperatures from solutions containing dissolved covellite and stibnite. There was no evidence, according to Gaines, to indicate that there was a mineral

phase in the system Cu-Sb-S that was comparable to enargite (Cu_3AsS_4) in composition and structure.

PREVIOUS WORK ON THE SYSTEM Cu-As-S

Prior to the investigations of Gaudin and Dicke (15) and Gaines (16) of the system Cu-As-S, there existed little information concerning the nature of the various phases such as tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$) which forms a complete isomorphous series with tetrahedrite; and the polymorphs, luzonite and enargite (Cu_3AsS_4). The mineral, lautite, was described by Schneiderhöhn (10) as having the composition CuAsS , but the existence of this substance as a distinct mineral type has yet to be confirmed.

Gaudin and Dicke synthesized tennantite varying in composition more extensively than tetrahedrite. Two distinct types, of high and low sulfur content, were observed on the basis of their filming characteristics. Only enargite appeared during the pyrosyntheses, with no trace of luzonite, indicating that the temperatures of crystallization were too high for the formation of luzonite, or that the isomorphous series extending from famatinite to luzonite was limited in arsenic content. Gaines succeeded in demonstrating that a complete solid solution series extended from famatinite (Cu_3SbS_4) to luzonite (Cu_3AsS_4). As a result of communicating with H. Sawada (17), Gaines reported that the transition temperature of formation of enargite from luzonite was about 275°C . Tennantite was produced by Gaines at high temperatures

from alkaline solutions; luzonite at low temperatures from acid or neutral solutions; and enargite from acid or neutral solutions at temperatures above 300°C.

PREVIOUS WORK ON THE SYSTEM Cu-Fe-S

The first serious investigation of the system Cu_2S -FeS according to Baykoff and Troutneff (18) was undertaken in 1906 by Röntgen during which he encountered the existence of 7 intermediate compounds. Shortly thereafter, Baykoff and Troutneff reported the presence of a complete solid solution series extending from Cu_2S to FeS at temperatures just below melting. The next group of investigators of the system Cu_2S -FeS were Carpenter and Hayward (19), who, in 1923, confirmed the earlier findings of Baykoff and Troutneff by observing no intermediate phases. They observed solid solutions containing as much as 92.5 percent by weight FeS in Cu_2S and as much as 50.0 percent by weight Cu_2S in FeS.

In 1934, Borchert (20) studied some of the unmixing and stability relations in the system Cu-Fe-S, using natural intergrowths of the phases chalcopyrite, bornite and pyrrhotite. He indicated that chalcopyrite and bornite enter into solid solution above 500°C and that chalcopyrite forms a solid solution with chalcopyrrhotite (CuFe_4S_6) above 450°C. Below 255°C chalcopyrrhotite was found to be unstable, and was transformed into cubanite at 235°C or valerite at 225°C. Solid solutions of chalcopyrrhotite and pyrrhotite were found to unmix at 550°C with complete unmixing at 350°C.

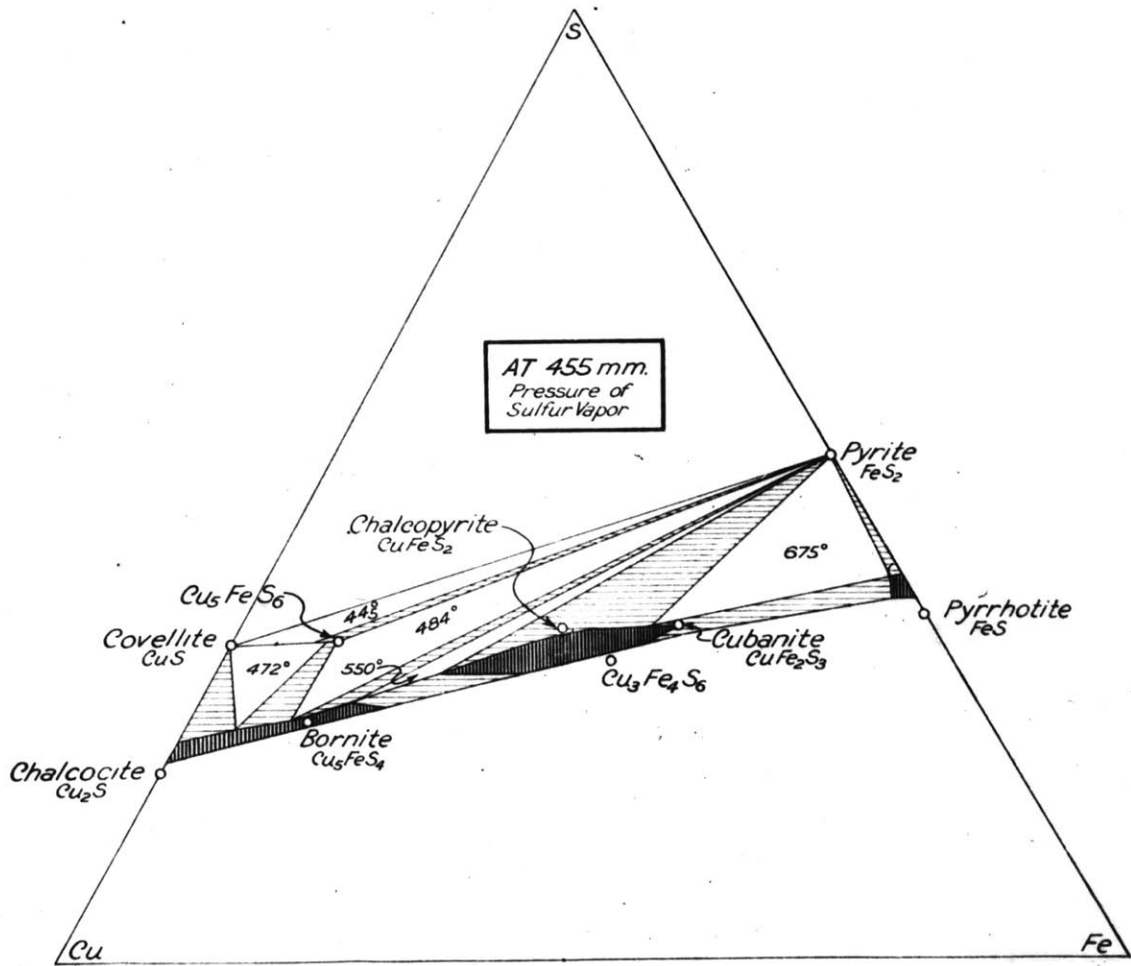
Chalcopyrite and bornite were found by Schwartz (21) to form extensive, but non-continuous solid solutions above the temperature, 475°C .

The first systematic study of the system Cu-Fe-S using only solid phases in equilibrium with a vapor phase, was performed by Merwin and Lombard (22) in 1937. Mattes composed of varying amounts of iron and copper sulfides were heated almost to melting and at a sulfur vapor pressure of 455 mm. The high-temperature phase relations which were obtained in detail are reproduced in Fig. 2. The phases synthesized were bornite, varying in composition from Cu_5FeS_4 to Cu_5FeS_6 , chalcopyrite (CuFeS_2) cubanite (CuFe_2S_3) and the compound $\text{Cu}_3\text{Fe}_4\text{S}_6$. Cubanite and chalcopyrite were found to enter into complete solid solution above 400°C . At this temperature, the chalcopyrite, according to Newton W. and M.J. Buerger (23) is disordered, and on cooling, reverts to the low ordered form by expelling cubanite or chalcopyrrhotite. Recent work by C.G. Cheriton (24) has shown that high-temperature chalcopyrite has a disordered sphalerite-type structure, which is capable of considerable solid solution.

The mineral valeriite is described in the Dana System of Mineralogy (8) as having a probable composition of $\text{Cu}_2\text{Fe}_4\text{S}_7$ or $\text{Cu}_3\text{Fe}_4\text{S}_7$ and of being massive and metallic, resembling pyrrhotite but exhibiting properties characteristic of graphite. The minerals cupropyrite (CuFe_2S_4) and chalcopyrrhotite (CuFe_4S_6) have been considered as types of cubanite.

Figure 2

Equilibrium phase diagram of the system Cu-Fe-S,
reproduced from Merwin and Lombard (22).



APPARATUS AND PROCEDURE

X-Ray Heating Powder Camera

The apparatus used in the investigation of the various phases at temperatures ranging from 30° to 350°C was an x-ray heating powder camera with built-in furnace assembly designed by M.J. Buerger, Newton W. Buerger, and Frank G. Chesley (25). The camera was well suited for the study of phase equilibria, since the photographic film could be removed for development without altering the specimen or temperature. The temperature of the furnace was regulated by a Weston wattmeter by varying the voltage input. The furnace was cooled by running water, which also provided a base-level temperature for raising the power input by the number of watts corresponding to the difference between the base-level and the desired temperature. The temperature was maintained constant to about 1 degree by using a voltage stabilizer. The apparatus is shown in operation in Fig. 3.

The furnace-temperature calibration was obtained by mounting pyrex capillaries containing substances with known melting points within the furnace. A plot of furnace temperature, ΔT , versus wattage (heat input) is shown in Fig. 4.

Preparation of Samples

1. Selection of Sulfides

For use as end-member sulfides in the various systems it was necessary to select pure materials having definite

Figure 3

X-ray heating-powder camera assembly in operation.

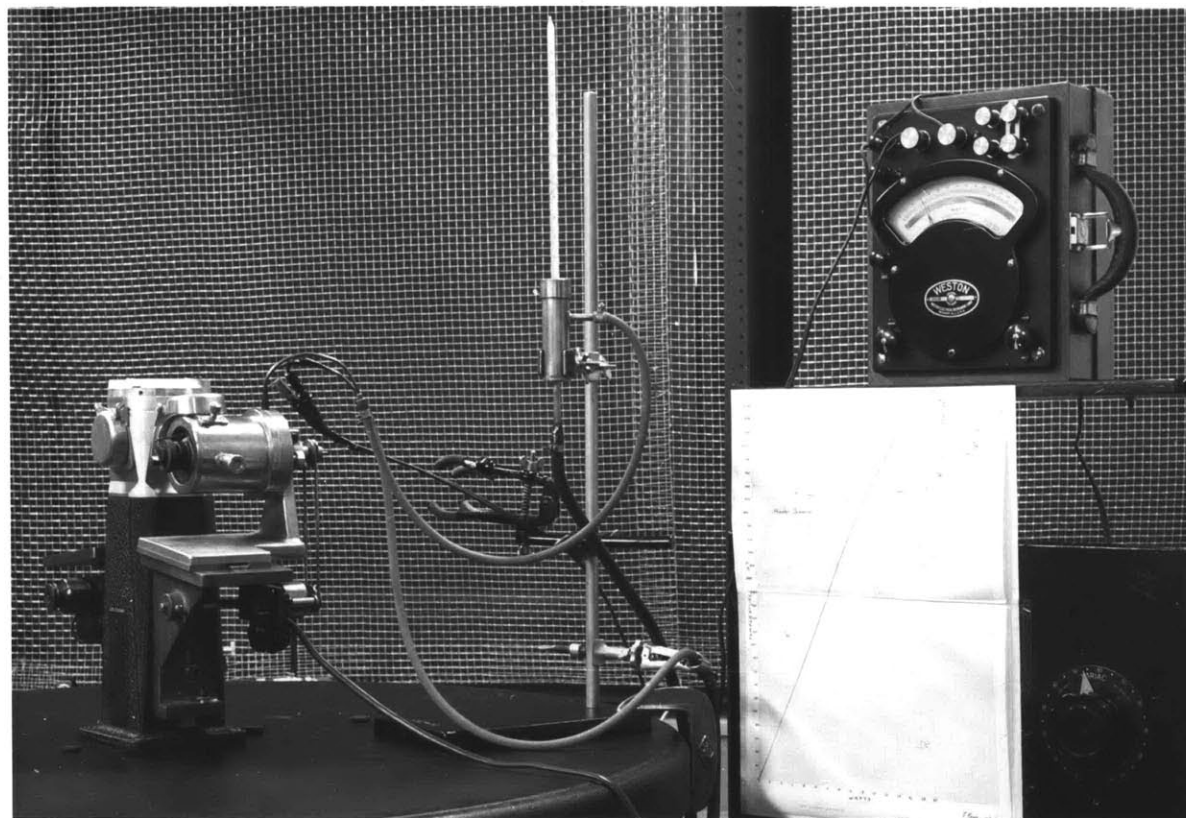
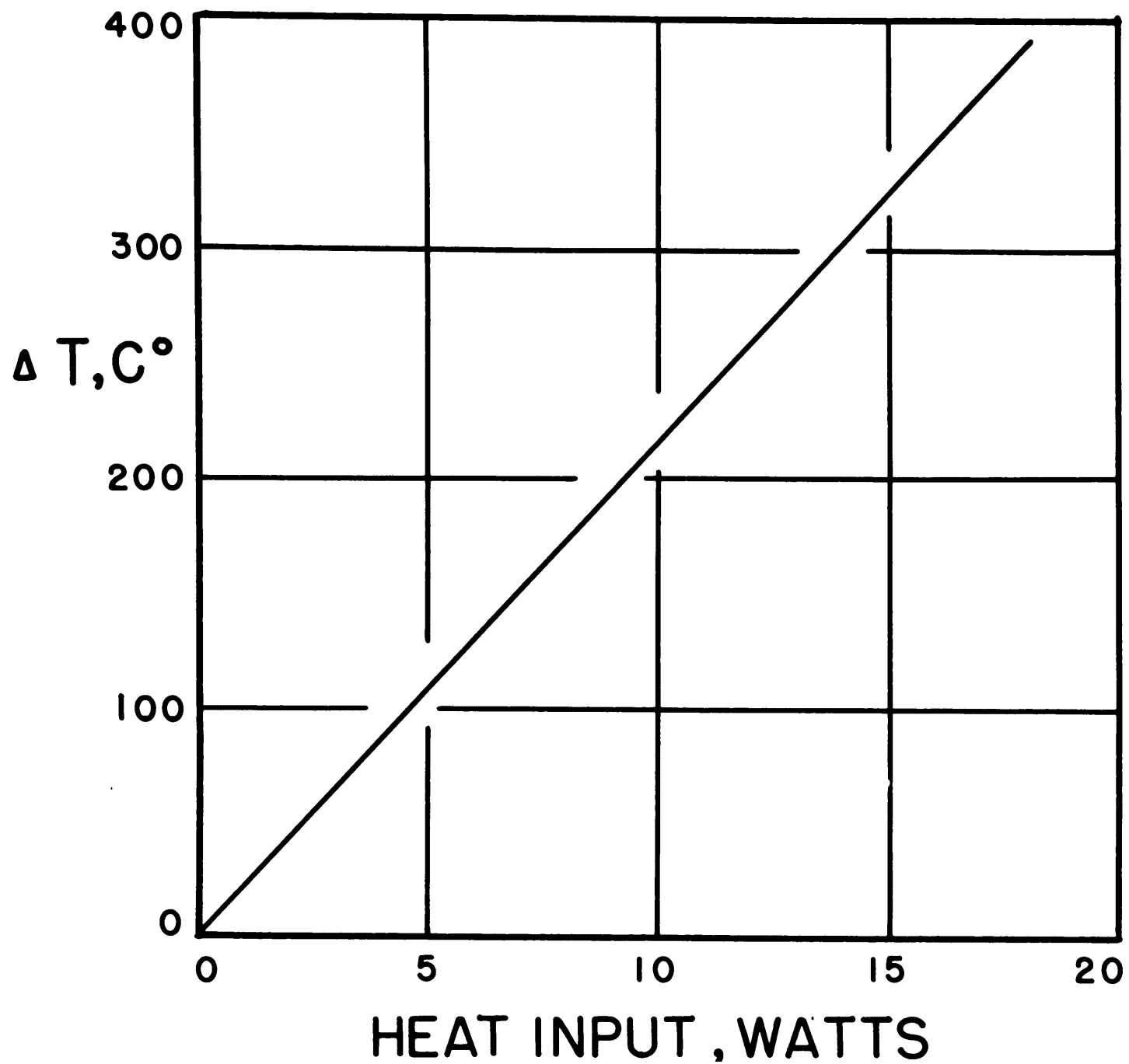


Figure 4
Furnace temperature calibration curve.



chemical compositions and physical properties.

a. Chalcocite, Cu_2S

It was found impossible to obtain a sufficient quantity of pure chalcocite from Bristol, Connecticut, the source of the mineral used by Newton W. Buerger during his investigation of the system $\text{Cu}_2\text{S}-\text{CuS}$. The Bristol chalcocite was found to invert very satisfactorily, compared with samples of synthetic Malinckrodt cuprous sulfide, which completely failed to invert at temperatures up to 150°C , and which also failed to react with covellite. Various samples of Butte chalcocite were found to contain appreciable iron and other impurities. Fortunately, information was obtained concerning the existence of some very pure chalcocite which had been collected from the Baltic Lode of the Champion Mine, at Keeweenau, Michigan by A.D. Wandke, whose thesis was concerned with the origin of chalcocite. A chemical analysis of this massive, white chalcocite revealed the presence of only 0.08 percent iron and a few ten-thousandths of a percent arsenic. Spectrographic plates run on samples of the Michigan and Bristol chalcocites were almost identical with regard to purity. Both types of chalcocite were found, in addition, to have similar thermal inversions. Furthermore, Wandke had been successful in synthesizing digenite by heating the Michigan chalcocite with native covellite. All of these factors recommended the use of the Michigan chalcocite as satisfactory for future investigations.

b. Stibnite, Sb_2S_3

The chemical analyses recorded by Doelter and Leitmeier (26) for samples of the mineral stibnite from various localities, served to indicate that material from Iyo Province, Japan was ideally Sb_2S_3 and uncontaminated by gangue. A sizable quantity of Iyo stibnite was subsequently obtained from the Harvard Mineralogy Collection. Spectrographic analysis of the material indicated that it was exceedingly pure, making it ideally suited as an end-member in the system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$.

c. Orpiment, As_2S_3

On the basis of spectrographic and x-ray analyses, a massive sample of Macadonian orpiment obtained from the M.I.T. mineral collection was chosen for work on the system $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$.

d. Covellite, CuS

The Malinkrodt analyzed cupric sulfide was found to be very satisfactory for further work on the system $\text{Cu}_2\text{S}-\text{CuS}$, since it was chemically pure and structurally identical with native covellite.

e. Pyrrhotite, FeS

Considerable difficulty was encountered in obtaining a large enough quantity of sufficiently pure troilite, a pyrrhotite having the ideal composition, FeS . All of the samples of pyrrhotite which had been investigated exhibited specific gravities that were lower than the calculated value for FeS . Baker's ferrous sulfide, granular, was found to be

the most desirable for use after it had been hand sorted and washed in dilute hydrochloric acid to remove any oxide coating that may have been present. The processed material was found spectrographically to contain less than 1 percent copper and nickel. Its x-ray powder photographs compared favorably with those obtained for natural samples of pyrrhotite and troilite. On the basis of the measured specific gravity of 4.73, the ferromagnetic pyrrhotite was believed to have the composition $\text{Fe}_{0.48}\text{S}_{0.52}$, which indicated that it was less deficient in iron than any of the other pyrrhotites that were available. Furthermore, the material was transformed from a superstructure to the simple basic structure at 135°C , as shown in Fig. 16. This seemed to be in accord with the evidence found by M.J. Buerger (27) for the existence of a superstructure in the ferromagnetic pyrrhotite region.

2. Method of Pretreating Samples

The methods used in the preparation of the samples were basically similar to those employed by Newton W. Buerger (3) during his investigation of the system $\text{Cu}_2\text{S}-\text{CuS}$. The adoption of the same basic methods also provided the necessary means for comparison of the four systems: $\text{Cu}_2\text{S}-\text{CuS}$, $\text{Cu}_2\text{S}-\text{FeS}$, $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ and $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$.

The individual samples, consisting of mixtures of the various pure sulfides and each weighing one gram, were ground in a power mortar for a period of 30 minutes to one hour to yield a grain size of approximately 300 mesh. Each

sample was then compressed at 1200 atmospheres in the form of a cylinder measuring one-quarter inch in diameter and about three-eighths inch in length. The cylinders were then annealed in a muffle furnace for a period of 12 hours at 110°C, i.e. 5° above the temperature at which chalcocite completely disorders. The individual cylinders were ground, compressed, and annealed again, as before, in order to insure complete homogeneity. For the samples in the system $\text{Cu}_2\text{S}-\text{FeS}$, the annealing temperature was raised to 150°C and an atmosphere of nitrogen was used to prevent oxidation. The samples were then maintained at room temperature for a period of several days to establish equilibrium.

3. Method of Preparing X-Ray Specimen Mounts

Each specimen was then ground and recast in the form of a rod measuring one millimeter in diameter and about fifteen millimeters in length. The specially constructed steel die used for this purpose is shown unassembled in Fig. 5 and assembled for use in Fig. 6. The die consists of four vertical sections, which, when mounted in the base by a lock screw, combine to form a rod-shaped mold. The mineral sulfide mixtures were placed in a steel funnel which was set over the die to introduce small amounts of the samples into the bore below. The sample was compacted in the die in a series of steps using a small hammer and pistons of several lengths. When the bore was filled with sample, the base and funnel were removed, the screw was released, and the four vertical sections separated one at a time, thus allowing the rod-

Figure 5

X-ray specimen-mount die, shown unassembled.

Figure 6

X-ray specimen-mount die, shown assembled and
with specimen carrier.



shaped specimen to drop onto a bed of absorbent cotton to prevent shattering.

This type of specimen mount seemed to be the only satisfactory means of obtaining x-ray photographs at the lower temperatures in the system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$. Pyrex capillary mounts such as were used by Newton W. Euerger for the system $\text{Cu}_2\text{S}-\text{CuS}$, were found to be unsatisfactory, since the glass scattering greatly increased the background intensity on the x-ray photographs. It was also found impossible to pack the capillaries uniformly. The rod-shaped mounts were not only uniform but composed of very closely packed grains, which was beneficial in bringing the samples rapidly to equilibrium. No oxidation was observed at any of the experimental temperatures for mounts in the systems $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ and $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$. However, oxidation was observed on samples of high FeS content in the system $\text{Cu}_2\text{S}-\text{FeS}$ at temperatures above 200°C . As a general precaution, the individual rods were precoated with silicone stopcock grease. All of the samples were investigated at temperatures at least 100°C below melting, so that the reactions involving intermediate phase formation could be assigned to the solid state. The experimental work on the individual systems was limited to the temperature range in which the vapor pressure of sulfur was negligible.

Procedure

1. Outline of Procedure

Each sample, in the form of a rod-shaped mount, was safely conveyed by means of the brass carrier (shown in Fig. 6) for insertion into the specimen holder of the x-ray powder heating camera. The specimen was centered and enclosed within the furnace and camera.

The base-level temperature of the water in the furnace cooling system was recorded and the wattage was raised to yield the desired furnace temperature. The specimen was pre-heated for periods ranging from 20 minutes to 2 hours, depending on the length of time that was required to establish equilibrium. The temperature was maintained constant during the x-ray exposure, usually a period of one to two hours. A Philip's tube with copper target, operated at 30 Kv and 15 ma, was used for the systems $\text{Cu}_2\text{S-Sb}_2\text{S}_3$, and $\text{Cu}_2\text{S-As}_2\text{S}_3$. A similar tube with iron target was used for the system $\text{Cu}_2\text{S-FeS}$, and was operated at 30 Kv and 13 ma. Following the exposure, the camera was detached from the base of the assembly. The film was removed and developed, and the camera was reloaded with film and remounted in preparation for the next run.

2. Equilibrium in the Systems and the Method of Attaining Equilibrium

The diagrams of the low temperature phases of the systems $\text{Cu}_2\text{S-CuS}$, $\text{Cu}_2\text{S-Sb}_2\text{S}_3$, $\text{Cu}_2\text{S-As}_2\text{S}_3$ and $\text{Cu}_2\text{S-FeS}$ included in this work should not be construed as equilibrium-

phase diagrams, since the total time allowed for annealing the samples was limited to only twenty-four hours. If the annealing time had been extended, additional series of solid solutions might have been formed between chalcocite and the other end-member sulfides covellite, stibnite, orpiment and pyrrhotite. In connection with the preparation of the diagrams of the systems $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$ and $\text{Cu}_2\text{S}-\text{FeS}$, shown in Fig. 8, 12, and 13, intense efforts were made to establish the positions of the transition lines between fields I and II and I and III under equilibrium conditions as follows:

A typical specimen was heated to the temperature at which digenite in field I was encountered. This temperature was recorded as being above the true conversion temperature. The specimen was then cooled to a lower temperature. If the x-ray photograph at that temperature indicated the presence of the phase in field II, for example, this temperature was noted as a temperature below that of conversion. By the process of alternately heating and cooling the specimen in the region between these two temperature limits the range was gradually reduced to five or ten degrees centigrade. The method is illustrated in Fig. 7 for the composition 93 percent by weight chalcocite - 7 percent by weight stibnite.

At the lower temperatures, the conversion process was observed to be highly reversible, but at the higher temperatures in the system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, the transformations to tetrahedrite and chalcostibnite were found to be

Figure 7

X-ray photographs of specimen containing
93 percent by weight chalcocite and
7 percent by weight stibnite.

95^o → 90^oC

93% chalcocite - 7% stibnite at 90^oC CuK 30KV 20ma 1.0hr. 7/11/52

100^oC → 95^oC

93% chalcocite - 7% stibnite at 95^oC CuK 30KV 20ma 1.0hr. 7/10/52

95^o → 100^oC

93% chalcocite - 7% stibnite at 100^oC CuK 30KV 20ma 1.1hrs. 7/10/52

90^o → 95^oC

93% chalcocite - 7% stibnite at 95^oC CuK 30KV 20ma 0.9hr. 7/10/52

80^o → 90^oC

93% chalcocite - 7% stibnite at 90^oC CuK 30KV 20ma 1.0hr. 7/10/52

R.T. → 80^oC

93% chalcocite - 7% stibnite at 80^oC CuK 30KV 20ma 0.9hrs. 7/10/52

R.T. → 110^oC

93% chalcocite - 7% stibnite at 110^oC CuK 30KV 20ma 0.9hrs. 7/9/52

R.T.

93% chalcocite - 7% stibnite at r.t. CuK 30KV 20ma 1.0hr. 7/2/52

irreversible; the phases failed to convert on cooling.

In addition to the fact that the annealing period was limited to only twenty-four hours, the diagram of the system $\text{Cu}_2\text{S}-\text{CuS}$, which has been reproduced in Fig. 1, cannot be considered as an equilibrium-phase diagram because of an apparent violation of the phase rule. On the diagram, along the field boundary line at twenty molar percent CuS , it appears that there are three phases - chalcocite, digenite and covellite in equilibrium. In any two component system in which the only variables are temperature and composition, three phases cannot coexist in equilibrium, except at a single fixed point, at which the system is invariant.

If one is to interpret from the diagram of the system $\text{Cu}_2\text{S}-\text{CuS}$, that the pure-digenite phase field is to extend below 47°C to room temperature, the field should have been gradually narrowed in the region of the "ideal" composition, Cu_9S_5 . However, on examining the x-ray photographs that were prepared by Newton W. Buerger for this system, the pure digenite field was not found to extend below 47°C .

On the basis of x-ray photographs alone, it is impossible to differentiate between high-temperature chalcocite and digenite, since all of the digenite reflections are present on photographs of high-temperature chalcocite. Therefore, the duplex phase field consisting of digenite and chalcocite could be an extension of the chalcocite solid-solution field. The corresponding fields designated as II on the diagrams of the systems $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$, and $\text{Cu}_2\text{S}-\text{FeS}$ are

described here as homogeneous chalcocite solid solutions.

RESULTS

Fields and Phases in the System $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$

On the basis of examining several hundred x-ray photographs of previously annealed compacts of chalcocite and stibnite, the diagram shown in Fig. 8 was constructed. Each dot on the diagram represents an x-ray photograph taken at the specified composition and temperature.

The following fields were encountered at low temperatures:

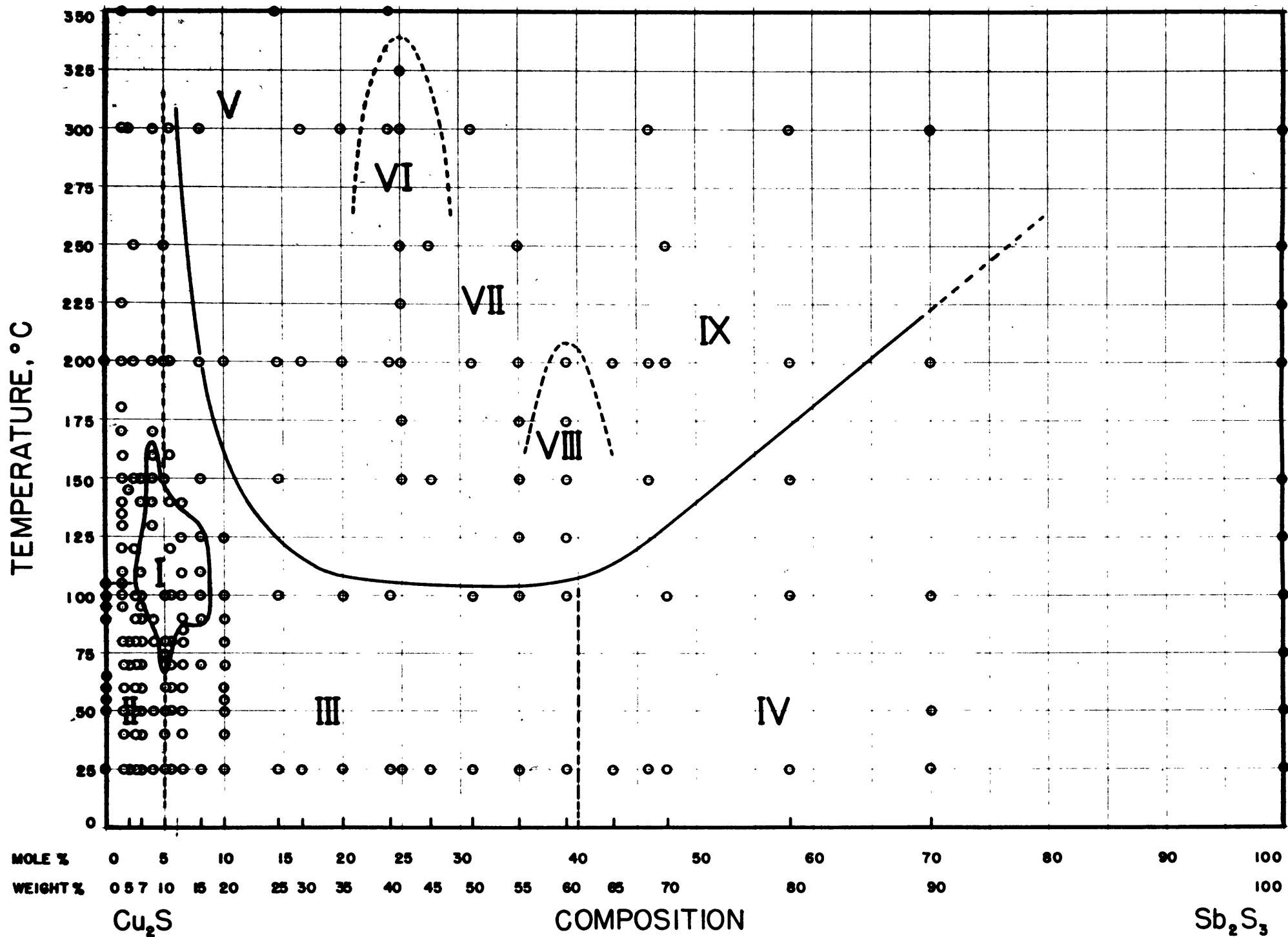
- I Stibiodigenite Solid Solution
- II Stibiochalcocite Solid Solution
- III α -Stibiodigenite Solid Solution Series
- IV α -Stibiodigenite Solid Solution + Stibnite
- V Chalcocite + Tetrahedrite (Stylotypite)
- VI Stylotypite Solid Solution
- VII Stylotypite + Chalcostibite
- VIII Chalcostibite Solid Solution
- IX Chalcostibite + Stibnite

The regions intermediate between phase fields I, II, III, IV and V, VI, VII, VIII and IX include additional solid solutions, which are structurally related to both the high- and low-temperature phases. The high-temperature phases failed to convert on cooling.

Discussion of the Fields and Phases of the System $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$

The stibiodigenite phase of field I is undoubtedly isostructural with ordinary cuprodigenite, which has been

Figure 8
Diagram of the system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$.



found in the system $\text{Cu}_2\text{S}-\text{CuS}$ by Newton W. Buerger. Stibiodigenite was found to exhibit a variation in composition of 3 - 8 molar percent Sb_2S_3 . The "ideal" composition, $\text{Cu}_{19}\text{SbS}_{11} = 19\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$, of the stibiodigenite solid solution was found to be stable in the temperature range from 67° to 147°C beyond which it was ultimately transformed into chalcocite and stylopyrite, which are present on the equilibrium melting diagram of the system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, that was constructed by Parravano and de Cesaris (14).

The stibiochalcocite phase of field II was observed as a homogeneous, white (weakly anisotropic to isotropic) phase in polished sections. With increasing, but minor amounts of Sb_2S_3 (about 2 percent), the low-temperature solid solution was gradually transformed into a phase structurally resembling high-temperature chalcocite.

The α -stibiodigenite solid solution series of field III refers to the collection of phases found in the region from 5 to about 40 molar percent Sb_2S_3 . These phases, which may be considered as the successors to the stibiochalcocite phase of field II, have resulted from the complete reaction of chalcocite and stibnite in the solid state. The polished sections made from typical members in the compositional range of the series appeared to be homogeneous, light gray, and isotropic. Typical members of the series are shown in Fig. 9 in relation to chalcocite, stibnite and sphalerite. The phases of the α -stibiodigenite series which lie nearest to stibiodigenite field I, exhibit x-ray patterns which can

Figure 9

Room temperature x-ray photographs of previously annealed specimens containing chalcocite and stibnite.

Chalcocite at R.T.

CuK 10/52

90% Chalcocite-10% Stibnite

at R.T.

CuK 10/52

87% Chalcocite-13% Covellite at R.T. (by N. Buerger, 6/40)

80% Chalcocite-20% Stibnite

at R.T.

CuK 10/52

70% Chalcocite-30% Stibnite

at R.T.

CuK 10/52

65% Chalcocite-35% Stibnite

at R.T.

CuK 10/52

60% Chalcocite-40% Stibnite

at R.T.

CuK 10/52

40% Chalcocite-60% Stibnite

at R.T.

CuK 10/52

Sphalerite at R.T.

CuK 10/52

Stibnite at R.T.

CuK 10/52

be indexed on the basis of a cubic-face-centered cell, 11 Angstroms in length; this is about twice the edge of the stibiodigenite cell. A sphalerite-type structure was encountered towards the end of the series on the approach to a metal to sulfur ratio of 1:1. Beyond about 40 molar percent Sb_2S_3 , increasingly less Sb_2S_3 is taken into the structure of the final member of the series.

On the x-ray patterns of the series, a high background intensity was encountered in the region of high θ . This effect may have been due to some kind of inherent atomic disorder in the samples, to structural deformation, or to the small particle size of the material.

The transformation of the low-temperature α -stibiodigenite phase into stypitpite is shown in Fig. 10. The transformation to chalcostibite, which occurs about 100°C lower than the transformation to stypitpite is shown in Fig. 11. The formation of the high-temperature solid solutions of chalcocite from the low-temperature phases takes place at still higher temperatures.

A plot of the temperatures of formation of the high-temperature equilibrium phases found in the system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ roughly parallels the melting curves exhibited by Parravano and de Cesaris for this system. Braune (28) developed a theory which tends to explain this. He demonstrated that the rate of diffusion in mixed crystals at the absolute temperature, T , was proportional to

Figure 10

X-ray photographs showing the transformation to stylumite.

300-350°C

60% chalcocite - 40% stibnite at 350°C CuK 30KV 20ma 1.5hrs. 8/29/52

R.T.

Tetrahedrite - Bingham, Utah R.T. CuK 30KV 15ma 1.7hrs. 9/19/52

R.T. → 300°C

60% chalcocite - 40% stibnite at 300°C CuK 30KV 20ma 1.3hrs. 8/28/52

R.T.

Tetrahedrite - R. Gaines, Harvard CuK 30KV 15ma 1.4 hrs. 8/3/52
(Synthetic)

300°C

58.5% chalcocite - 41.5% stibnite at 300°C CuK 30KV 15ma 1.7hrs. 9/2/52

250°C

58.5% chalcocite - 41.5% stibnite at 250°C CuK 30KV 15ma 1.4hrs. 9/2/52

225°C

58.5% chalcocite - 41.5% stibnite at 225°C CuK 30KV 15ma 1.7hrs. 9/2/52

175°C

58.5% chalcocite - 41.5% stibnite at 175°C CuK 30KV 15ma 1.8hrs. 9/2/52


R.T.


58.5% chalcocite - 41.5% stibnite at Room Temperature CuK 30KV 15ma 1.6hrs. 9/1/52

Figure 11


X-ray photographs showing the transformation to chalcostibite. X-ray photographs of 94 percent by weight chalcocite and 6 percent by weight orpiment.

R.T. 
Chalcostibite Paratanz, Morocco. CuK 30KV 20ma 1.7 hrs. 8/17/52


200°C 
40% chalcocite - 60% stibnite at 200°C CuK 30KV 20ma 1.8 hrs 6/30/52


175°C 
40% chalcocite - 60% stibnite at 175°C CuK 30KV 15ma 1.4 hrs. 6/30/52


150°C 
40% chalcocite - 60% stibnite at 150°C CuK 30KV 15ma 1.7 hrs. 6/30/52


125°C 
40% chalcocite - 60% stibnite at 125°C CuK 30KV 15ma 1.6 hrs. 6/30/52

R.T. 
40% chalcocite - 60% stibnite at r.t. CuK 30KV 20ma 1.7 hrs 6/30/52

110°C 
99% chalcocite - 6% orpiment at 110°C CuK 30KV 15ma 1.0 hr 9/24/52

100°C 
99% chalcocite - 6% orpiment at 100°C CuK 30KV 15ma 1.0 hr. 9/24/52

80°C 
99% chalcocite - 6% orpiment at 80°C CuK 30KV 15ma 1.3 hrs. 9/24/52

R.T. 
99% chalcocite - 6% orpiment at R.T. CuK 30KV 15ma 1.0 hr. 9/23/52

$$\exp\left(-\frac{b^2 T_m}{T}\right),$$

where b is a constant having a numerical value of approximately 1, and T_m is the absolute temperature of melting. This relation was developed by relating the process of diffusion to that of melting in conjunction with Lindemann's theory that melting occurs when the average amplitude of the atomic vibrations reaches a critical value.

A minor change in the x-ray photographs of stibnite was observed at 210°C, namely the addition of a reflection corresponding to a spacing of 3.3 Angstroms. The amorphous, red stibnite phase, metastibnite was not encountered during this investigation. According to G.M. Schwartz (29) metastibnite is transformed into stibnite at 200°C under pressure.

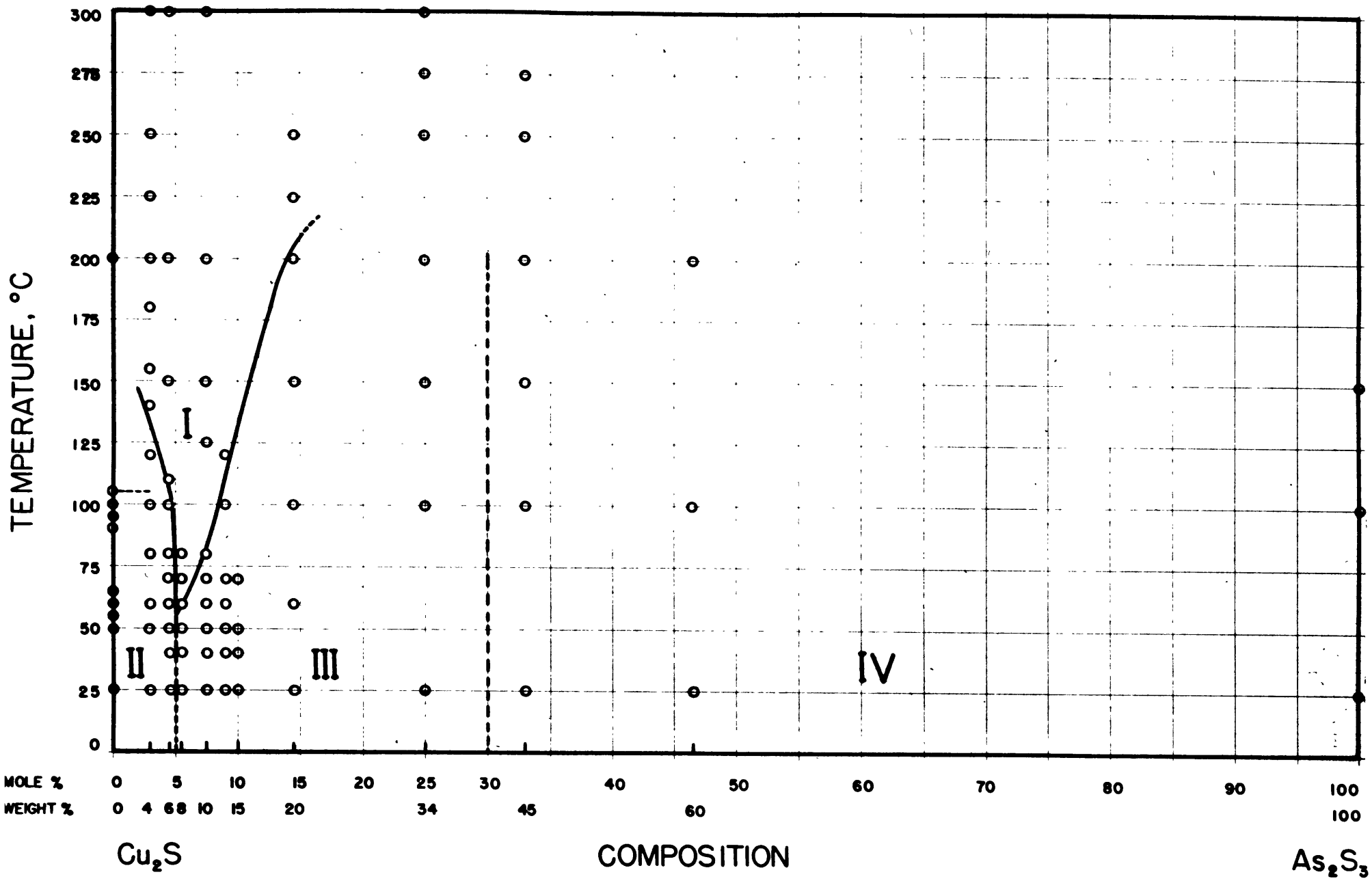
Fields and Phases in the System $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$

The results of the investigation of the system $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$ are valid only in the temperature region below 150°C owing to the high volatility of the mineral orpiment at higher temperatures. For this reason also the high-temperature phase tennantite (Cu_3AsS_3), was not synthesized. The diagram of the low-temperature phases in the system $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$ is shown in Fig. 12.

The following fields were encountered at low temperatures:

Figure 12

Diagram of the system $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$.



- I Arsenodigenite Solid Solution
- II Arsenochalcocite Solid Solution
- III α -Arsenodigenite Solid Solution Series
- IV α -Arsenodigenite Solid Solution + Orpiment

Discussion of the Fields and Phases of the System $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$

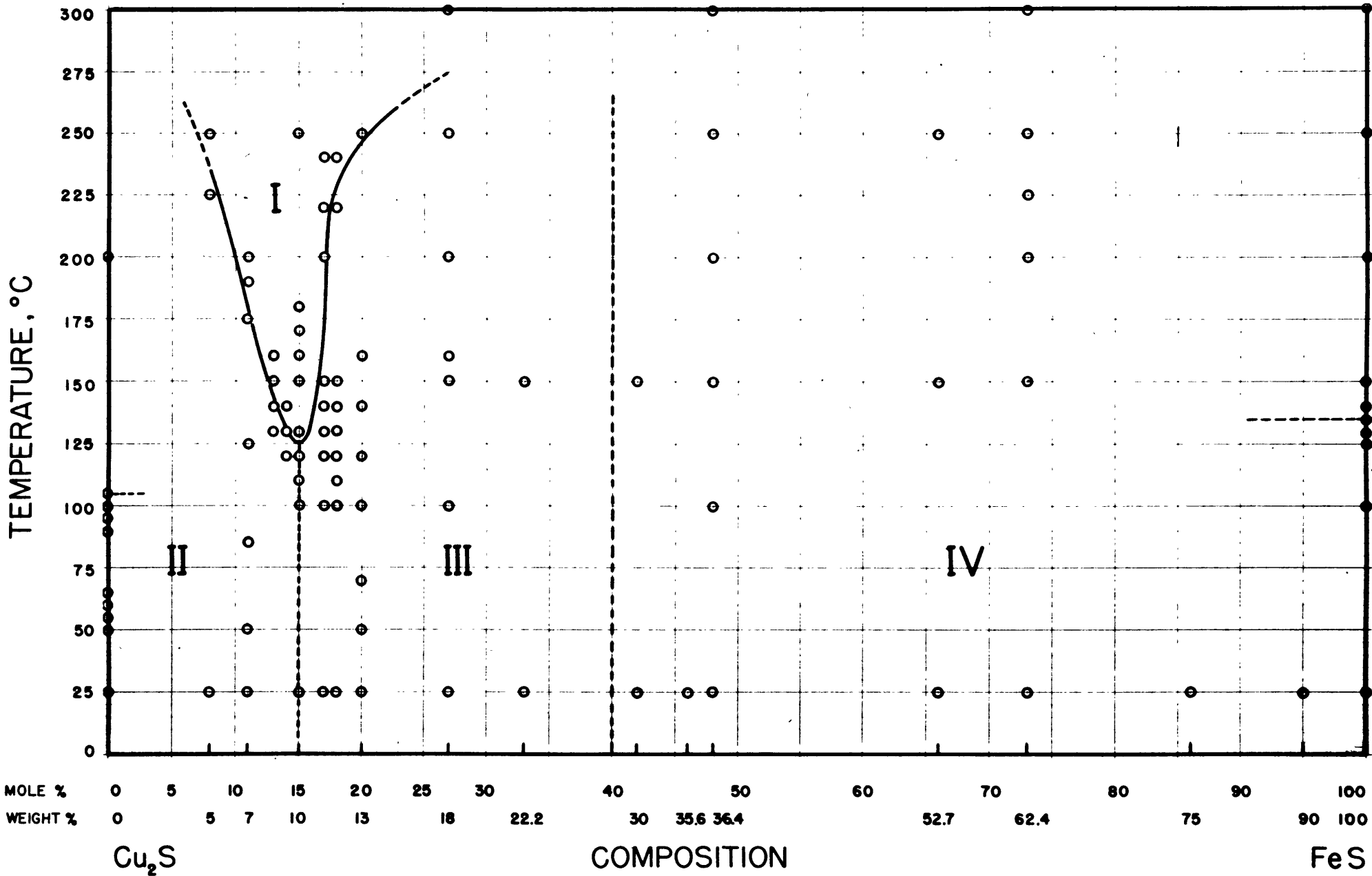
The minimum temperature of formation of the "ideal" arsenodigenite ($\text{Cu}_{19}\text{AsS}_{11}$) lies about 12 degrees C lower than the corresponding temperature of formation of stibio-digenite. This phenomenon may be due to the fact that the melting point of orpiment is considerably lower than that of stibnite.

Complete solid solution series must extend between the arseno- and stibio-digenite and chalcocite phases, since the phases found in fields I, II, and III in the systems $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$ and $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ are isostructural. However, the low-temperature α -arsenodigenite series appear to be less extensive, due apparently to a slower rate of diffusion, but this seems to conflict with the melting-temperature relations which have been cited thus far. Differences in the structures or chemical bonding of orpiment and stibnite may be responsible for the effect.

Fields and Phases in the System $\text{Cu}_2\text{S}-\text{FeS}$

The diagram of the phases in the low-temperature region of the system $\text{Cu}_2\text{S}-\text{FeS}$ is shown in Fig. 13. This diagram was constructed from a collection of x-ray photographs taken of compacts of chalcocite and pyrrhotite that had been

Figure 13
Diagram of the system $\text{Cu}_2\text{S}-\text{FeS}$.



previously annealed at 150°C for 24 hours. The location of the samples was guided by a general knowledge of the high-temperature equilibrium data that was available for the system Cu-Fe-S.

The following fields were encountered at low temperatures:

- I Ferrodigenite Solid Solution
- II Ferrochalcocite Solid Solution
- III α -Ferrodigenite Solid Solution Series
- IV α -Ferrodigenite Solid Solution + Pyrrhotite

Discussion of the Fields and Phases in the System Cu_2S -FeS

The minimum temperature of formation of the "ideal" ferrodigenite $\text{Cu}_{34}\text{Fe}(3.0-2.8)\text{S}_{20}$ is very much higher than those found for the antimony, arsenic and copper analogues. The "ideal" digenite was found to contain 5 molar percent less FeS than CuS even though both copper and iron are divalent in this case and exhibit similar chemical properties on the whole. In the region of lowest FeS content in field III the α -ferrodigenite series exhibits x-ray patterns which can be indexed on the basis of a cubic face-centered cell with an edge of about 11 Angstroms, just as in the case of the corresponding members of the α -stibio- and arseno-digenite series. This phase is identical with the high-temperature disordered phase of bornite (shown in Fig. 14) which was also obtained by Alfred J. Frueh (30). The α -ferrodigenite series have remained stable at room temperature, hence it is

Figure 14

X-ray photographs of 93 percent by weight chalcocite and 7 percent by weight pyrrhotite. X-ray photographs showing the transformation from low- to high-temperature bornite.

200°C

93% chalcocite - 7% pyrrhotite at 200°C FeKd 30KV 13ma 1.0hr 10/20/52

175°C

93% chalcocite - 7% pyrrhotite at 175°C FeKd 30KV 13ma 1.0hr 10/20/52

150°C

93% chalcocite - 7% pyrrhotite at 150°C FeKd 30KV 13ma 1.0hr 10/20/52

80°C

93% chalcocite - 7% pyrrhotite at 80°C FeKd 30KV 13ma 1.0hr 10/19/52

R.T.

93% chalcocite - 7% pyrrhotite at R.T. FeKd 30KV 13ma 1.0hr 10/18/52

125°C

Bornite, Bristol at 125°C

FeKd

11/7/52

R.T.

Bornite, Bristol at R.T.

FeKd

11/3/52

not known for certain that they are disordered. The high-temperature form of bornite could not be preserved on quenching, but always reverted to low-temperature bornite. The x-ray photographs of 82 percent by weight chalcocite and 18 percent by weight pyrrhotite in Fig. 16 should be compared with the bornite transformation shown in Fig. 14. In Fig. 14, the conversion of chalcocite and pyrrhotite to ferrodigenite is also presented. Some low-temperature x-ray photographs of the system $\text{Cu}_2\text{S}-\text{FeS}$ are shown in Fig. 15.

If the period of annealing had been longer, the ferrodigenite series might have been extended with a more complete assimilation of pyrrhotite to include prototypes of chalcopyrite, cubanite and possibly Merwin's compound ($\text{Cu}_3\text{Fe}_4\text{S}_6$).

Figure 15

Room temperature x-ray photographs of
previously annealed specimens of
chalcocite and pyrrhotite.

90% Chalcocite-10% Pyrrhotite at R.T. FeK 11/52

82% Chalcocite-18% Pyrrhotite at R.T. FeK 11/52

Bornite, Bristol, Conn. at R.T. FeK 11/52

78% Chalcocite-22% Pyrrhotite at R.T. FeK 11/52

66% Chalcocite-34% Pyrrhotite at R.T. FeK 11/52

48% Chalcocite-52% Pyrrhotite at R.T. FeK 11/52

42% Chalcocite-58% Pyrrhotite at R.T. FeK 11/52

24% Chalcocite-76% Pyrrhotite at R.T. FeK 11/52

10% Chalcocite-90% Pyrrhotite at R.T. FeK 11/52

Pyrrhotite at R.T. FeK 10/52

Figure 16

X-ray photographs of 82 percent by weight chalcocite and 18 percent by weight pyrrhotite. X-ray photographs of the transformation from low to high-temperature pyrrhotite.



GENERAL DISCUSSION

Comparison of the Digenite Phases of the Systems: $\text{Cu}_2\text{S}-\text{CuS}$, $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$, and $\text{Cu}_2\text{S}-\text{FeS}$

The compositions of the digenite phases in each of the above systems are as follows:

<u>System</u>	<u>Minimum Temperature</u>	<u>Ideal Composition</u>	<u>Ratio Metal:Sulfur</u>
$\text{Cu}_2\text{S}-\text{CuS}$	47°C	Cu_9S_5	9.00:5.00
$\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$	55°C	$\text{Cu}_{19}\text{AsS}_{11}$	9.10:5.00
$\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$	67°C	$\text{Cu}_{19}\text{SbS}_{11}$	9.10:5.00
$\text{Cu}_2\text{S}-\text{FeS}$	125°C	$\text{Cu}_{34}\text{Fe}(3.0-2.8)\text{S}_{20}$	9.25-9.20:5.00

There appears to be a correlation between the minimum temperature of formation of digenite having the ideal compositions and the melting points of the pure sulfides in each case, which are as follows:

CuS	-	220°C (Reported decomposition temperature)
As_2S_3	-	300°C
Sb_2S_3	-	545°C
FeS	-	1163°C

For the ideal compositions, the metal to sulfur ratio is approximately 9 to 5 in each case. A type of ferro-cupro-digenite is known to occur in nature as a result of the replacement of bornite by chalcocite. The minimum temperature of formation of this phase was recorded by G.M. Schwartz (31)

as 100°C which is about halfway between the minimum temperatures recorded for the cupro- and ferro-digenites above.

The α -digenite series found in the systems $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$ and $\text{Cu}_2\text{S}-\text{FeS}$ in the regions bordering of the digenite fields (I), are isostructural with the series observed on x-ray photographs that were prepared by Newton W. Buerger for the system $\text{Cu}_2\text{S}-\text{CuS}$. The digenite phase in each case has been found to revert to a chalcocite solid solution, or to α -digenite at lower temperatures.

The digenite phases can vary extensively in composition by assimilating more sulfur or cuprous copper atoms at the higher temperatures. There also seems to be little limitation on the nature of the substituted polyvalent metal atoms. Solid-state reactions between chalcocite and other minerals such as galena, bismuthinite, and numerous lead, antimony, arsenic, iron, and bismuth sulfosalts and complex sulfides should be possible.

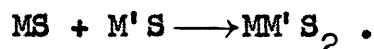
Mechanism of Formation of the Intermediate Phases

The formation of the various intermediate phases, such as digenite, that were synthesized in the systems $\text{Cu}_2\text{S}-\text{CuS}$, $\text{Cu}_2\text{S}-\text{FeS}$, $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ and $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$ involved reactions in the solid state at temperatures far below melting. The reaction phenomena might well be described as solid solution, but this term should be used only in the strict thermodynamic sense to denote the resultant intermediate phase, since its formation can be achieved not only by diffusion in the solid state, but also through the action or solidification of a

liquid phase.

The interactions of the various sulfides and chalcocite in this case appear to be comparable with the observed diffusion in such systems as $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$, and $\text{AgCl}-\text{NaCl}$, etc., where there is a common anionic constituent of negligible mobility. In this respect Jost (32) has drawn an analogy between diffusion in solid "ionic-type" crystals and the diffusion of ions in the solution of an electrolyte. However, in the case of electrolytic solutions, the cations all move towards the negative pole, but in the case of diffusion in solid "ionic-type" crystals, the mobile constituents, metal ions, flow in opposite directions in order to preserve electric neutrality.

The equation for the general case involving the formation of an intermediate sulfide phase, where the metal constituents diffuse as "ions" and the mobility of the sulfur atoms is almost negligible, is as follows:



The equations for flow of metal "ions", \underline{M} and \underline{M}' , of concentrations \underline{C} and \underline{C}' in the presence of both a concentration gradient and a potential gradient $\frac{\partial \phi}{\partial x}$ are:

$$J_M = - u_M \left(kT \frac{\partial C}{\partial x} - Ze_M C \frac{\partial \phi}{\partial x} \right)$$

$$J_{M'} = + u_{M'} \left(kT \frac{\partial C'}{\partial x} - Ze_{M'} C' \frac{\partial \phi}{\partial x} \right)$$

where \underline{u} is the ionic mobility of the cation, equal to the

velocity in unit electric field in e.u. and \underline{Ze} is the charge on the cation. The latter term in the equations for flow refers to the current caused by the diffusion potential ϕ which arises as a result of the different mobilities of the metal ions. Since $\underline{C+C'}$ is constant,

$$\frac{\partial C}{\partial x} = - \frac{\partial C'}{\partial x} .$$

Electric neutrality requires that the total rate of transport be equal to zero, hence setting

$$J_M = - J_{M'} ,$$

the potential gradient,

$$\frac{\partial \phi}{\partial x} = - \frac{(u_{M'} - u_M)}{(u_M C Z e_M + u_{M'} C' Z e_{M'})} \frac{\partial C'}{\partial x} kT .$$

Substituting for $\frac{\partial \phi}{\partial x}$ in the equations for flow,

$$J_M = - J_{M'} = - kT \frac{\partial C}{\partial x} u_M u_{M'} \frac{(C Z e_M + C' Z e_{M'})}{(u_M C Z e_M + u_{M'} C' Z e_{M'})} ,$$

which is identical to the Nernst equation for the diffusion of ions in solutions of electrolytes. From the Nernst-Einstein relation for the coefficient of diffusion,

$$D_{MM'} = u_M u_{M'} kT \frac{(C Z e_M + C' Z e_{M'})}{(u_M C Z e_M + u_{M'} C' Z e_{M'})}$$

is finally obtained. By allowing $\underline{N_M}$ to represent the fraction

$$\frac{CZ_{e_M}}{CZ_{e_M} + C'Z_{e_{M'}}$$

and similarly for $\underline{N_{M'}}$, an average mobility is obtained:

$$u_{MM'} = \frac{u_M u_{M'}}{N_M u_M + N_{M'} u_{M'}} .$$

Consequently, the coefficient of diffusion may be represented as follows:

$$D_{MM'} = u_{MM'} kT .$$

The equation for the coefficient of diffusion has been presented to illustrate the effects of the mobilities of the two types of metal atoms on the overall rate of diffusion for the case where the mobility of the sulfur atoms is so slight as to be neglected. On the basis of diffusion experiments on chalcocite and covellite, Wandke (7) concluded that digenite was formed as the result of not only the diffusion of "copper ions out of chalcocite", but also by the "diffusion of copper ions into covellite". This mechanism, alone, on the basis of what is now known concerning diffusion in similar systems, could not result in electric neutrality, since the covellite phase would contain excess positive charge and the chalcocite phase would be negatively charged. The increases in volume and weight of the chalcocite phase observed by Wandke during his diffusion experiments can be explained more satisfactorily by the simultaneous diffusion or chemically-equivalent interchange of cuprous and cupric

ions, from chalcocite and covellite, respectively.

If the theory of cationic diffusion is correct, the coefficient of diffusion should be obtainable from a knowledge of the individual coefficients of self-diffusion, whereby,

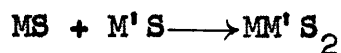
$$u_M = \frac{kT}{D_M} .$$

The mobilities could also be obtained from the determination of the electrolytic conductivities and transference numbers obtained from an appropriate galvanic cell. The coefficients of self-diffusion of copper in chalcocite were found to be of the order of 10^{-9} - 10^{-7} cm²/sec at about 100°C by M.L. Jensen (33). Chalcocite was also shown to have exceptionally low activation energies for electrolytic conduction and diffusion, of the order of a few kilocalories per mole. During this investigation, no direct determinations of the coefficients of diffusion were made, but a few experiments were carried out to determine the relative rates of formation of the intermediate phases, which are functions of the coefficients of diffusion. It was felt that such data would have a direct bearing on the formation of the intermediate phases in ore deposits.

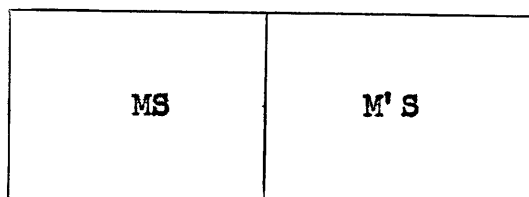
The method used to determine the relative rates of formation of the intermediate phases in the systems studied, was adopted essentially from Tammann and Rocha (34). Fine powders, about 250-300 mesh, of the pure sulfides were compressed into single pellets, each consisting of one-half

chalcocite and one-half either covellite, stibnite, orpiment, or pyrrhotite. Each pellet measured one-quarter inch in diameter and about three-eighths inch in length. The four pellets, representing the four systems studied, were placed in one arm of a long, U-shaped pyrex glass tube. The pellets were separated from each other by means of short glass rods. The tube assembly was connected to a slow, steady stream of nitrogen gas, and then placed within a muffle furnace for runs at 130° and 200°C for different lengths of time.

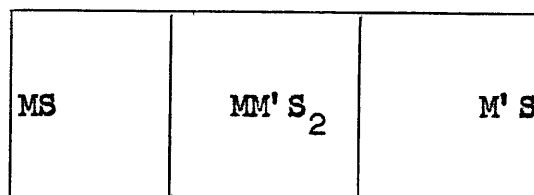
Since each pellet was composed of the end-member sulfides in each of the systems studied, it was expected that after time t , had elapsed at temperature, T , the long cross-sections of the pellets would be in reality a model of the phase distribution contained along the horizontal of the equilibrium diagrams at temperature, T . Assuming for the sake of simplicity that only one intermediate phase is formed as a result of the reaction:



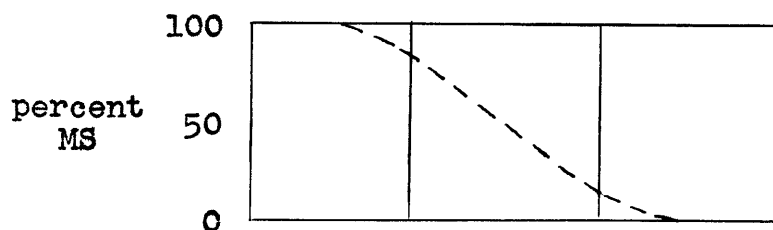
and representing the initial state of the pellet composed of sulfides, MS and M'S,



the final state of equilibrium after heating the pellet at temperature, T , for time, t , would be,



The concentration of MS is assumed to be as follows:



In accordance with Fick's Law, the quantity of ions or

atoms, \underline{M} , diffusing across the interface in time \underline{dt} ,

$$dn = D_M \cdot A \frac{\Delta C}{x} \cdot dt$$

where $\underline{D_M}$ is the diffusion coefficient, \underline{A} , the area of cross-section and $\frac{\Delta C}{x}$, the concentration gradient in the intermediate phase, assumed to be linear. Since \underline{dn} corresponds to a proportionate increase in the thickness, \underline{dx} , of the intermediate phase,

$$dn = b \cdot A \cdot dx .$$

Substituting for \underline{dn} , and integrating,

$$\frac{1}{2}x^2 = D_M \cdot \frac{\Delta C}{b} \cdot t .$$

Since the quantities $\underline{D_M}$, \underline{b} , and \underline{C} will not be determined separately, they can be consolidated into \underline{k} , the rate constant, measured in $\text{cm}^2 \text{sec}^{-1}$. The thickness of the intermediate phase

$$x = (2k \cdot t)^{\frac{1}{2}} .$$

Therefore, if the previous assumptions are correct, a plot of the thickness of the intermediate phase versus the square root of time should yield essentially a straight line.

Following each run, the individual pellets were mounted in lucite, cut lengthwise normal to the interface, and polished. The results obtained for pellets heated at 200°C are shown in Fig. 17, 18, 19, 20, 21 and 22. In the following table are listed the data that were obtained from the

Figure 17

Intermediate phase formation in the system
 $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$: 200°C, 24 hrs. (C-chalcocite,
S-stibnite).

Figure 18

Intermediate phase formation in the system
 $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$: 200°C, 64 hrs.



Figure 19

Intermediate phase formation in the system
 $\text{Cu}_2\text{S}-\text{CuS}$: 200°C , 48 hrs. (C-chalcocite,
Co-covellite).

Figure 20

Microscopic detail of intermediate digenite
phase in the system $\text{Cu}_2\text{S}-\text{CuS}$. The entire field
shown consists of isotropic digenite that is
replacing chalcocite on the left and covellite
on the right.



Figure 21

Intermediate phase formation in the system
 $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$: 200°C, 64 hrs. (C-chalcocite,
O-orpiment).

Figure 22

Intermediate phase formation in the system
 $\text{Cu}_2\text{S}-\text{FeS}$: 200°C, 64 hrs. (C-chalcocite,
P-pyrrhotite).

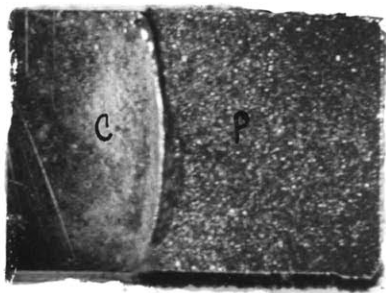
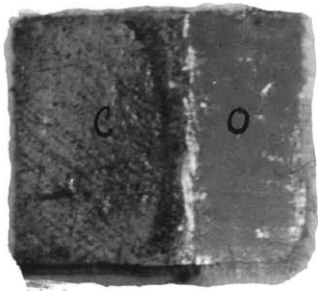


Table of Results of Interdiffusion Experiments

<u>MS-M'S System</u>	<u>Temp.</u>	<u>Time</u>	<u>Thickness of Intermediate Phase (s)</u>	<u>Nature of Intermediate Phase (s)</u>	<u>Nature of Chalcocite</u>	<u>Nature of M'S</u>	<u>k, cm² sec⁻¹ Rate Constant</u>
Cu ₂ S-CuS	200°C	48 hrs	1.2 mm	Digenite	Weakly	Strongly	2.0 x 10 ⁻⁶
		48 "	1.15 "	(½ replaced	Aniso-	Aniso-	
		36 "	0.8 "	chalcocite,	tropic,	tropic,	
		30 "	0.6 "	½ replaced	white.	blue.	
		24 "	0.4 "	covellite),			
	130°C	72 "	1.1 "	Isotropic,		5.2 x 10 ⁻⁸	
		48 "	0.8 "	white.			
Cu ₂ S-Sb ₂ S ₃	200°C	64 hrs	1.1 mm	Chalco-	Weakly	Strongly	5.3 x 10 ⁻⁷
		48 "	0.9 "	stibite,	Aniso-	Aniso-	
		24 "	0.4 "	digenite,	tropic,	tropic,	
	130°C	72 "	0.1 "	and residual	blue.	white.	1.4 x 10 ⁻⁸
	48 "	0.05 "	stibnite.				
Cu ₂ S-As ₂ S ₃	200°C	64 hrs	0.8 "	Digenite and	Weakly	Aniso-	3.9 x 10 ⁻⁷
		48 "	0.6 "	residual	Aniso-	tropic,	
		24 "	0.3 "	orpiment.	tropic,	yellow-	
	130°C	72 "	0.05 "		blue.	white.	9.5 x 10 ⁻⁹
		48 "	0.01 "				
Cu ₂ S-FeS	200°C	96 hrs	Irregular	Digenite and	Weakly	Aniso-	-----
		64 "	boundaries	iridescent	Aniso-	tropic,	
	130°C	24 "	with sep-	phase (s)	tropic,	gray-	-----
		72 "	aration of	unidentified.	white.	white.	
	48 "	initial					
			phases.				

experiments. The values of the rate constants, k , that were obtained from the graph in Fig. 23, were found to be of a high order of magnitude compared with various alloy systems. No values of k were obtained for the system $\text{Cu}_2\text{S}-\text{FeS}$ due to the physical separation of the primary phases and the irregular phase boundaries. However, the rates were observed to be much smaller than those obtained for the other systems.

In the systems $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$, and $\text{Cu}_2\text{S}-\text{FeS}$, the intermediate phases were found to differ in texture and reflectivity. However, the textures of chalcocite and covellite were preserved during the formation of cuprodigenite (Fig. 20). If both the copper and sulfur constituent atoms in this case diffused at appreciable rates, it is doubtful that the original structures would have been preserved.

From the crude assumption that:

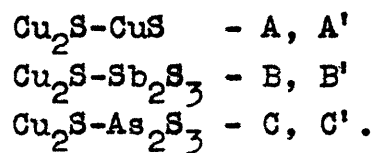
$$k_1 = C \exp\left(-\frac{\Delta E}{kT_1}\right), \text{ and}$$

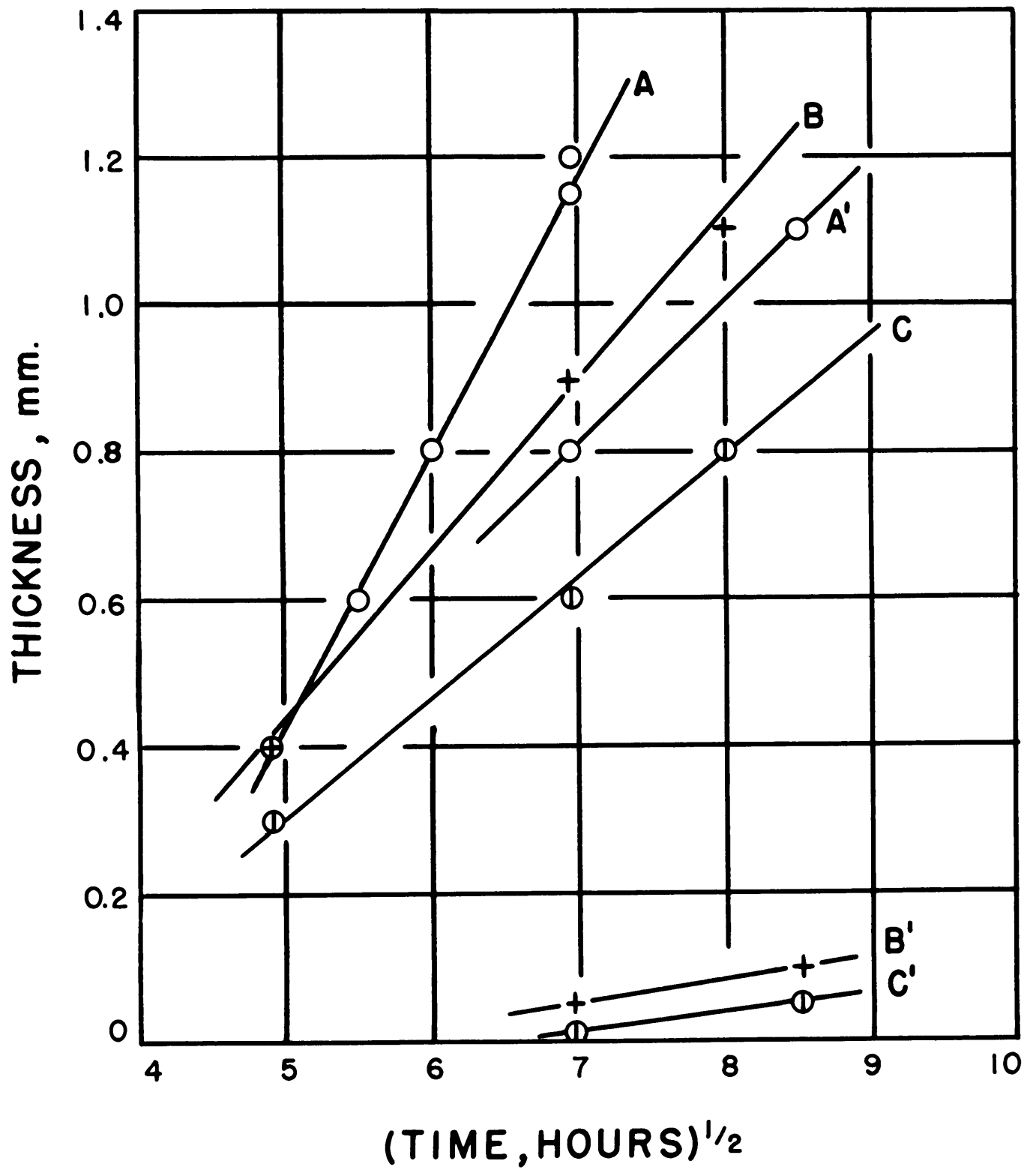
$$k_2 = C \exp\left(-\frac{\Delta E}{kT_2}\right)$$

the average activation energy, ΔE , of intermediate phase formation in the systems $\text{Cu}_2\text{S}-\text{CuS}$, $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, and $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$ was calculated to be 7.9 kilocalories per mole. The net conclusions to be drawn from these experiments are that the rates of intermediate phase formation at low temperatures are appreciable and that considerable importance must be attached to the role of solid-state diffusion in ore deposits.

Figure 23

Graph showing rate-constant curves obtained by plotting the intermediate phase thickness versus time at temperatures 200°C and 130°C for systems:





Some Aspects Relating to the Crystal Structure of Digenite

Considerable significance must be attached to a knowledge of the crystal structure of digenite, since this phase is the prototype of not only the members of the α -digenite series, but also the stable forms of bornite, tetrahedrite, etc. The first investigation of the structure of digenite, $\text{Cu}_{1.8}\text{S}$, was carried out by Rahlfs (5), who synthesized it by heating metallic copper in an excess of sulfur. Not one of the sets of intensities calculated by Rahlfs from nineteen different hypothetical structures for digenite was in complete agreement with the intensities that were measured from x-ray powder photographs of digenite at 170°C . Rahlfs concluded that digenite had essentially an anti-fluorite structure, with sulfur atoms at 000 , $0\frac{1}{2}\frac{1}{2}$, etc., 4 copper atoms at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, and the remainder statistically distributed over a large number of undetermined sites.

In 1949, mixtures of digenite and minor chalcocite were precipitated from aqueous solutions of CuCl charged with H_2S at ordinary temperatures by Hogart and Molé (35). On the basis of x-ray powder photographs of the mixtures, Hogart and Molé concluded that the low temperature form of digenite has a structure that is identical with one, proposed earlier by Rahlfs, in which the sulfur atoms are found at 000 , $0\frac{1}{2}\frac{1}{2}$, etc., 4 coppers at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, and the remaining 3.2 copper atoms statistically distributed over the positions, \underline{uuu} , where $\underline{u} = \frac{2}{3}$.

L.V. Azaroff of the Department of Geology, utilizing

the same technique as Hogart and Molé, synthesized digenite which was found to yield an x-ray pattern that was identical with those synthesized during the investigations described in this thesis of the systems $\text{Cu}_2\text{S-CuS}$, $\text{Cu}_2\text{S-FeS}$, $\text{Cu}_2\text{S-Sb}_2\text{S}_3$ and $\text{Cu}_2\text{S-As}_2\text{S}_3$ at varying temperatures and compositions. Furthermore, this pattern was essentially the same as the one described by Rahlfs (5) from which the latter was unable to completely solve the structure. A recheck of the intensities computed by Rahlfs, including the structure adopted by Hogart and Molé, indicated that they were essentially correct as tabulated. By postulating the basic structure proposed by Hogart and Molé and varying the uuu parameters slightly, it was still found impossible to arrive at a suitable structure.

The net conclusion to be drawn from these facts is that the structure of digenite, synthesized by these three wholly different methods is apparently the same and still undetermined.

Tunell and Adams (36) discovered that the reflections having strong and medium intensities on x-ray patterns obtained from a single crystal of orthorhombic bornite from Cornwall, could be indexed on a cubic face-centered cell that was slightly smaller than the digenite cell. A structure was proposed for bornite in which 4 sulfur atoms are found at 000 , $0\frac{1}{2}\frac{1}{2}$, etc., 4 metal atoms are statistically distributed over $\frac{111}{444}$, and the remaining 2 metal atoms statistically distributed over $\frac{333}{444}$. The agreement between

the observed and calculated intensities was excellent. The observed relative intensities, correcting for multiplicity, of the bornite used by Tunell and Adams were similar to the measured intensities recorded for a powdered sample of bornite from Magma, Arizona by Harcourt (37). The relative intensities that were observed in these cases were found to be different from those observed from samples of bornite from Bristol, Connecticut, which were used by Alfred J. Frueh (30) during his investigation of thermal disorder and also during the course of this work. The fundamental intensities of the Bristol bornite seem to be very similar to those of the digenite synthesized during this investigation.

It may be that there are at least two kinds of bornite, found at ordinary temperatures, a type having the fundamental structure designated by Tunell and Adams, and a type having a structure that is more similar to that of digenite.

Geological Significance of the Investigation

As a result of the x-ray investigations of the solid phases of the systems $\text{Cu}_2\text{S}-\text{CuS}$, $\text{Cu}_2\text{S}-\text{FeS}$, $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ and $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$, the phases of ferrodigenite, stibiodigenite, and arsenodigenite have been discovered. Since the rates of formation of the digenite phases by diffusion in the solid state have been found to be high in the laboratory, it is obvious that similar intermediate phases can develop in ore deposits containing chalcocite at moderate to great depths.

The role of solid-state diffusion shortly after the deposition of ore bodies is significant at the prevailing temperatures of deposition, and equilibrium is probably established in a relatively short time. The role of solid-state diffusion during thermal metamorphism and following the reworking of deposits by solutions, should be appreciable. In cases where the "order of solubility" does not appear to be a usable criterion for replacement, solid-state diffusion may have been responsible for the formation of the intermediate phases. Sales and Meyer (38), reporting on the effect of post-ore dike intrusion on Butte minerals, showed fields which suggested the "progressive replacement of bornite by invasion of chalcocite" while the formation of the bornite was actually due to the "thermal metamorphism of a pyrite-bearing chalcocite ore". The distinction between primary and secondary digenite may also be difficult to ascertain, since digenite might be preserved by quenching solid solutions formed from the cooling of melts. Some

typical photographs of digenite that has resulted from the replacement of bornite by chalcocite have been reproduced in Fig. 24 from Edwards (39) and in Fig. 25 from Oosterbach (40).

On the basis of the results obtained for the system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ and from the similar chemical properties of antimony and bismuth, it appears very likely that chalcocite and bismuthinite, Bi_2S_3 , would react in the solid state to form bismodigenite, klaprotholite, $\text{Cu}_6\text{Bi}_4\text{S}_9$, cuprobismuthite, CuBiS_2 , and wittichenite, Cu_3BiS_3 . Furthermore, it seems very plausible that the reactions which have been achieved with chalcocite could be duplicated with acanthite, Ag_2S , which disorders thermally and forms solid solutions with chalcocite as a result of solid-state diffusion.

Since the rates of diffusion in the case of intermediate phase formation have been demonstrated to be most probably an average of the rates of self-diffusion of the metal atoms in their respective sulfides, the rates of self-diffusion of the antimony, arsenic, iron, and copper atoms in stibnite, orpiment, pyrrhotite and covellite might be sufficiently great to allow for such rapid diffusion as has been observed in the laboratory. Reactions at low temperatures between these sulfides and others, like galena, which is composed of highly polarizable lead atoms, may be possible. Similarly, interactions between sulfosalts and complex sulfides composed of such atoms might occur until equilibrium is established. More detailed observations of ore specimens containing intermediate phases, such as the sulfosalts and

Figure 24

A graphic intergrowth of blue chalcocite (light gray) replacing bornite (dark gray). White areas are pyrite residuals. North Lyell, Tasmania.
Reproduced from A.B. Edwards (39).

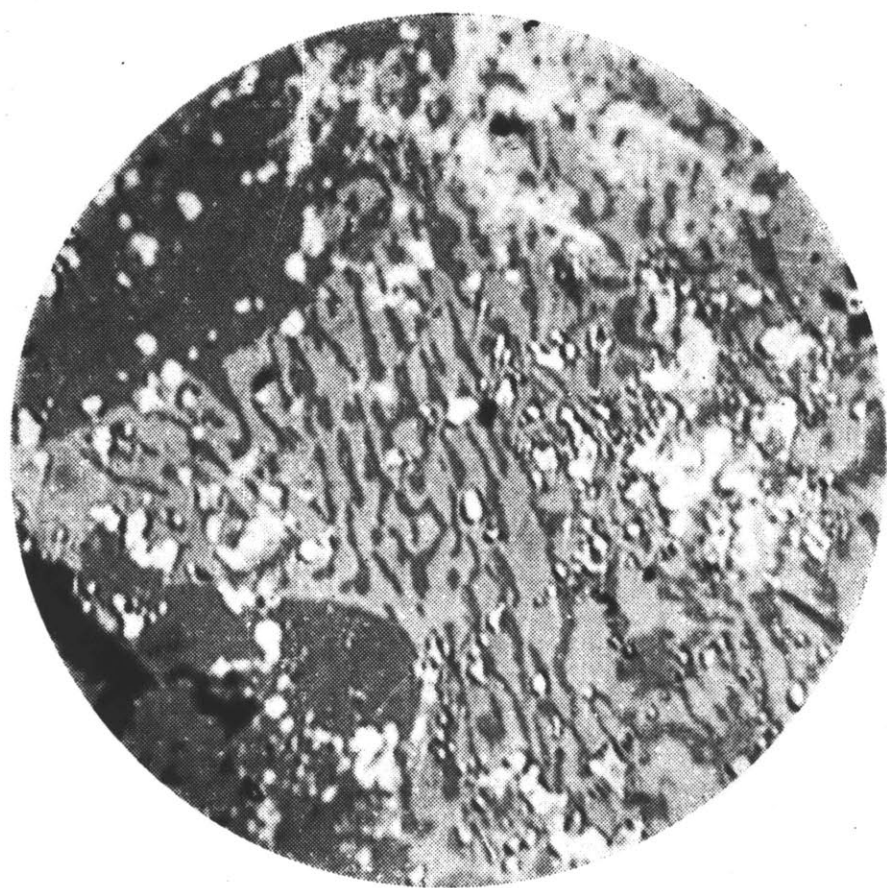
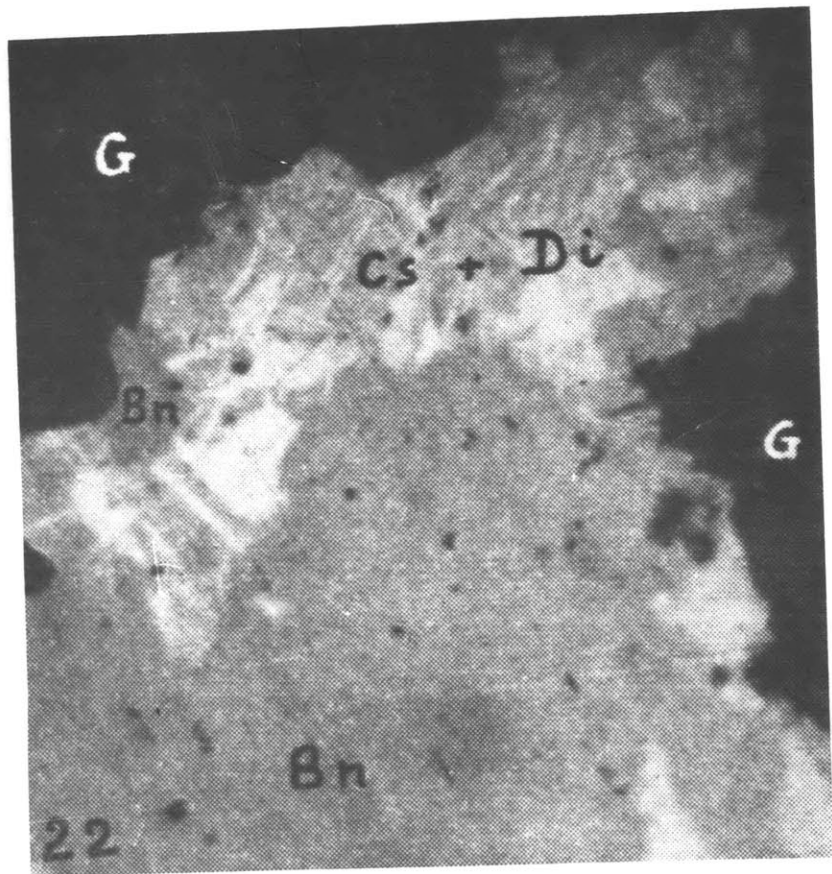


Figure 25

Replacement of bornite (Bn) by white (Cs) and blue (D1) chalcocite. Gangue (G) is black. Katanga. Reproduced from R. Oosterbosch (40).



complex sulfides, may serve to indicate that these phases were formed in completely closed systems. The prevalence of these intermediate phases and the corresponding rarity of such minerals as stibnite, orpiment, and bismuthinite in the same deposits may be due partly to complete assimilation in the solid state.

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BIOGRAPHICAL NOTE

Virginia F. Ross was born in Queens County, New York City on November 9, 1927, the daughter of Charles Henry and Mary Zane Franklin.

Education:

She attended Newtown High School, Elmhurst, New York from 1941-1944;

Queens College, Flushing, New York from 1944-1948, and was graduated with a B.S. degree in Chemistry;

Boston University, Boston, Massachusetts from 1948-1949, and was graduated with an A.M. degree in Geology.

She enrolled in the Department of Geology at Massachusetts Institute of Technology in September, 1950 for studies leading to the doctorate degree.

Professional experience and training were obtained as a:

Laboratory Assistant in Chemistry, Queens College, 1945-1948
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On August 26, 1950, she married John Ross.

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Professional Affiliations

Mineralogical Society of America, American Crystallographic Association, and Sigma Xi.