THE AMERICAN MINERALOGIST, VOL. 55, JANUARY-FEBRUARY, 1970

PHASE RELATIONS OF THE CU-S SYSTEM AT LOW TEMPERATURES: STABILITY OF ANILITE

NOBUO MORIMOTO AND KICHIRO KOTO, *Institute of Scientific and Industrial Research, Osaka University, Osaka, Japan.*

ABSTRACT

Anilite, digenite and synthetic samples of the composition range $Cu_{1.70}S$-$Cu_{1.82}S$ have been studied by the X-ray diffraction and microscopy. At room temperature, the stable phases in the range of composition studied are djurleite ($Cu_{1.97}S$), anilite ($Cu_{1.75}S$) and covellite (CuS). Above 70°±3°C, anilite decomposes to high digenite and covellite.

The digenite-type solid solution usually appears in synthetic experiments with composition between $Cu_{1.765}S$ and $Cu_{1.79}S$ at room temperature as indicated by Roseboom (1966), but its composition range occasionally extends from $Cu_{1.75}S$ to $Cu_{1.80}S$. The cell dimensions are irrationally related to the cubic subcell of high digenite, varying with composition. The synthesis and crystallographic studies of the digenite-type solid solution indicate that the solid solution is metastable at room temperature and decomposes to mixtures of anilite and djurleite.

Natural digenite always contains a small amount of iron and is considered to be stable only in the Cu-Fe-S system.

INTRODUCTION

In recent studies on the phase relations of the Cu-S system, Djurle (1958) and Roseboom (1966) confirmed four phases stable at room temperature. They are chalcocite (Cu_2S), djurleite ($Cu_{1.97}S$), digenite-type solid solution[1] and covellite (CuS). Roseboom (1966) indicated that the digenite-type solid solution is stable in the composition range $Cu_{1.765}S$-$Cu_{1.79}S$ at room temperature and that the Cu-poor limit is not affected by temperature, while the Cu-rich limit changes to $Cu_{1.83}S$ at 83°C where the digenite-type inverts to the high-temperature form. Morimoto and Kullerud (1963) found three polymorphs of digenite; high digenite, low digenite and transitional metastable digenite. The high digenite is cubic with $a = 5.57$ Å and the other polymorphs are superstructures of the high digenite.

Roseboom (1966) admitted, in the study of the digenite-type solid solution, that the strong lines in the powder patterns of the solid solution can be indexed by assuming cubic symmetry with a cell edge of about 5.56 Å. He observed, however, anomalous displacements of weak lines with change of composition, which he described as follows:

> . . . digenite of $Cu_{1.765}S$ composition is indexed [on the basis of cubic symmetry] following Morimoto and Kullerud. When a unit cell was obtained from the (10, 10, 0) peak, the (119) and (991) peaks were found to be about 0.1° to 0.2°

---

[1] This corresponds to the *digenite solid solution* by Roseboom (1966). This phase is, however, metastable at room temperature and different from natural digenite as explained later. We call it *digenite-type solid solution* or simply *digenite-type phase* in this paper.

> 2θ higher than their calculated positions. For digenite of $Cu_{1.79}S$ composition, the (555), (10, 0, 0) and (10, 10, 0) peaks were shifted to smaller 2θ values by a small amount but the peaks labelled (119) and (991) were shifted in the *opposite direction* and were about 0.4° and 0.6° 2θ away from their calculated positions.

Two possible explanations were considered by Roseboom for the line displacements: presence of metastable polymorphs or deviation from the cubic symmetry. By confirming that samples X rayed four hours after annealing showed the same displacements as those X rayed after four years at room temperature, he precluded the former possibility and assumed pseudocubic symmetry for the digenite-type solid solution.

Donnay, Donnay and Kullerud (1958), by single crystal work, found a pseudocubic cell for synthetic digenite with an edge five times the literature value of a synthetic phase of digenite-type. They attributed the absence of many reflections to the pseudocubic twinning of rhombohedral crystals. Because the rhombohedral cell is metrically cubic, however, the line displacements described by Roseboom cannot be explained on the basis of rhombohedral symmetry.

Since anilite was found in nature and was determined to be a compound of the Cu-S system with the composition $Cu_{1.75}S$ (Morimoto, Koto and Shimazaki, 1969), which is very close to the sulfur-rich limit of the digenite-type solid solution, it was necessary to elucidate the phase relation between anilite and the digenite-type solid solution.

In the present investigation, syntheses of anilite and the digenite-type solid solution were carried out in order to elucidate the phase relations of the Cu-S system at relatively low temperatures. In the study of the phase relations, the reason for the anomalous displacements of the weak reflections of the digenite-type solid solution with change of composition was clarified. The relationship between anilite and natural digenite is also discussed on the basis of the results of the electron-probe analysis and the synthesis of digenite.

EXPERIMENTAL

Except for natural minerals, the samples used in this investigation were synthesized dry from mixtures of sulfur and copper in the composition range $Cu_{1.70}S$-$Cu_{1.82}S$. Copper of 99.999 percent purity was obtained in rods from the American Smelting and Refining Co. Freshly prepared filings were used for all experiments. Oxide film on the surface of the rod was first removed by filing. Sulfur 99.999 percent pure was also obtained as grains from the same company. The mixtures were enclosed in evacuated silica tubes and kept for 72 hours at 500°C. They were annealed for one week (most of them at 300°C, some at 600°) and rapidly cooled to room temperature. The products consist of small single crystals of $0.01\sim0.3$ mm in size, which were examined by the X-ray powder and precession methods using Cu$K\alpha$ radiation (1.5418 Å). Some single crystals were examined at 50° to 100°C by the precession method. The microscopic method was also employed to determine existing phases in synthetic samples.

EXPERIMENTAL RESULTS

Four different phases, djurleite, digenite-type solid solution, anilite, and covellite, were found in the synthetic samples in the range $Cu_{1.70}S$-$Cu_{1.82}S$ (Table 1). The X-ray powder method and the reflection microscope were not suitable for detection of existing phases in the synthetic samples, because anilite changes to the digenite-type solid solution by grinding and polishing (Morimoto et al. 1969). The determination of phases in synthetic samples were, therefore, mainly made by the X-ray single crystal method, though covellite was detected by the microscope. "Blaubleibender" or "blue-remaining" covellite (Moh, 1964) was not encountered in the present study.

A few single crystals were picked in each synthetic sample and examined by the X-rays. The results on the single crystals did not necessarily show all existing phases in the synthetic sample, but it was possible to obtain probable phase relations among the four phases appearing in the synthetic samples. As described later, the composition of the members of the digenite-type solid solution was determined by the position of the superstructure reflections on their single crystal patterns.

Synthetic samples richer in sulfur than $Cu_{1.72}S$ (CS-62 and CS-65), obtained by rapid cooling from 300°C, were found to be a mixture of the digenite-type phase of $Cu_{1.765}S$ composition, which was the most Cu-poor member in the solid solution by Roseboom (1966), and covellite. The samples of $Cu_{1.75}S$ composition, cooled rapidly from 300°C (CS-56) and cooled slowly from 300°C to room temperature (CS-55), were also in many cases a mixture of the digenite-type phase ($Cu_{1.765}S$) and covellite. However, the mixtures of anilite and djurleite were often obtained with covellite (CS-49 and CS-17). In one sample (CS-51), the digenite-type phase appeared without covellite. The difference between the digenite-type phase with covellite and without covellite found in samples of $Cu_{1.75}S$ composition will be discussed later. Synthetic samples of $Cu_{1.77}S$ and $Cu_{1.78}S$ compositions were found to be the digenite-type phases without other phases or to be a mixture of anilite and djurleite in an epitactic relation (CS-73 and CS-76). When the copper content was more than $Cu_{1.80}S$, the samples became a mixture of the digenite-type phase of $Cu_{1.79}S$ composition, which was the most Cu-rich member in the solid solution by Roseboom (1966), and djurleite. One crystal from the sample of $Cu_{1.80}S$ (CS-10), rapidly cooled from 600°C, gave a single phase of the digenite-type without djurleite. This phase will be described in the next section in more detail.

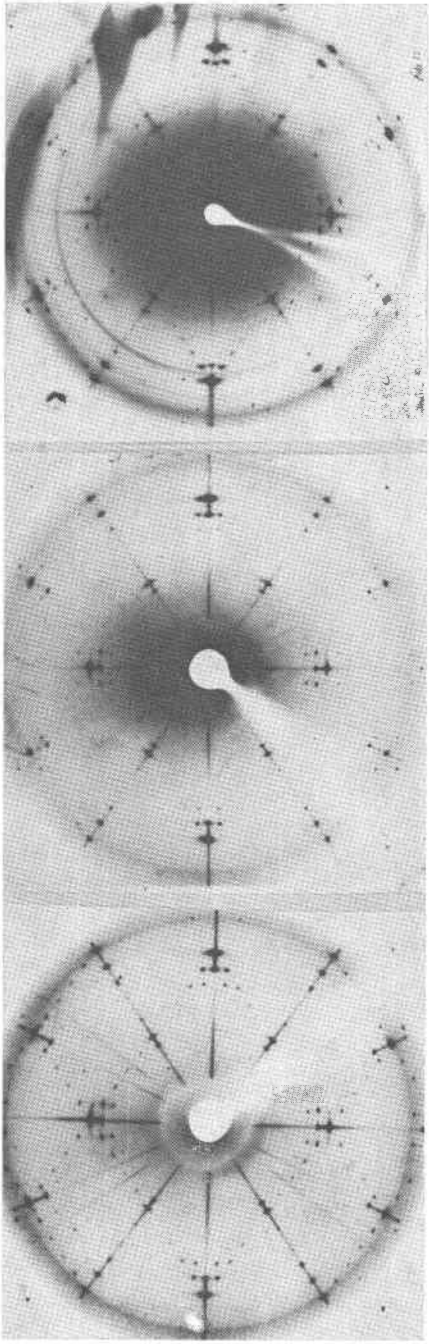
The results of these experiments are in good agreement with those by Roseboom (1966), except for the appearance of anilite. For the determination of the phase relations of anilite and the digenite-type solid solution, additional experiments were carried out. Before describing these experiments, however, we shall discuss the crystallographic properties of the digenite-type solid solution and explain the reason for the anomalous displacements of superstructure reflections.

DIGENITE-TYPE SOLID SOLUTION

Digenite-type phases with compositons $Cu_{1.75}S$ (CS-51), $Cu_{1.78}S$ (CS-76) and $Cu_{1.80}S$ (CS-10) were synthesized as single crystals at 300°C or 600°C. Their precession photographs $(1\bar{1}0)_0^*$ (Fig. 1) show characteristic patterns of the metastable transitional digenite of cubic symmetry with many absent reflections (Morimoto and Kullerud, 1966). The main strong reflections common to the three photographs of Figure 1 refer to the cubic cell of high digenite with $a \sim 5.57$ Å (the *a*-type structure). The superstructure reflections are quite different on the three photographs. In Figure 1(a), the superstructure reflections divide the repeat of the main reflections into five equal intervals along the $<111>^*$ direction, resulting in a supercell of cubic symmetry with $a = 27.79$ Å. This photograph is the same as that obtained by Donnay, Donnay and Kullerud (1958). In Figure 1(b), the superstructure reflections appear displaced. The interval between the main reflection and its nearest superstructure reflection is no longer 1/5 of the repeat of the main reflections along the $<111>^*$ direction, but is 1/5.5 of this repeat. In Figure 1(c) the corresponding interval is 1/6 of the repeat and the edge of the cell becomes six times that of the high digenite subcell.

The reciprocal coordinates defining the positions of the superstructure reflections of the digenite-type phases are generally given as $(h \pm n\delta t, k \pm n\delta t, l \pm n\delta t)$, where h, k and l are integers and refer to the high-digenite subcell, n is an integer (usually one, two or three) and δt represents a nonintegral positive number. If we regard the superstructure reflections as satellite reflections of the nth order of a main reflection (h, k, l), δt is the interval between the main reflection and its satellite reflection of first order expressed as a fraction of the repeat of the main reflections. The values of δt are, therefore, 1/5, 1/5.5 and 1/6 for the digenite-type phases of $Cu_{1.75}S$, $Cu_{1.78}S$ and $Cu_{1.80}S$ compositions respectively. The structure type of the digenite-type phases is conventionally expressed by the value Na of the cell edge in terms of the high-digenite subcell, where N is equal to $1/\delta t$. The values of N (Table 1) are easily obtained from the positions of main and superstructure reflections in the precession or powder patterns. The digenite-type phases are hereafter called Na-type according to their value of N.

In conclusion the digenite-type solid solution has the digenite-like structure of cubic symmetry which is a superstructure of high digenite.



(a) (b) (c)

FIG. 1. Precession photographs $(1\bar{1}0)_0^*$ of synthetic digenite-type phases with compositions $Cu_{1.73}S$ (CS-51)(a), $Cu_{1.78}S$ (CS-76)(b), and $Cu_{1.80}S$ (CS-10) (c).

TABLE 1. SYNTHETIC EXPERIMENTS ON THE SAMPLES OF THE COMPOSITION RANGE OF $Cu_{1.70}S$-$Cu_{1.82}S^a$

(a) Starting from mixtures of elements

Sample No.	Composition	Temperature and time	Result
CS-62	$Cu_{1.70}S$	500°C 3 days 300°C 7 days	cv, dgt (5.2)
CS-65	$Cu_{1.72}S$	500°C 3 days 300°C 7 days	cv, dgt (5.2)
CS-17	$Cu_{1.75}S$	500°C 3 days 300°C 7 days	cv, anl+dj
CS-49	$Cu_{1.75}S$	500°C 3 days 300°C 7 days	cv, dgt (5.2), anl+dj
CS-51	$Cu_{1.75}S$	500°C 3 days 300°C 7 days	dgt (5.0)
CS-55	$Cu_{1.75}S$	500°C 3 days 300°C 7 days	cv, dgt (5.2)
CS-56	$Cu_{1.75}S$	500°C 3 days 300°C 7 days	cv, dgt (5.2)
CS-73	$Cu_{1.77}S$	500°C 3 days 300°C 7 days	dgt (5.4), anl+dj
CS-76	$Cu_{1.78}S$	500°C 3 days 300°C 7 days	dgt (5.5), anl+dj
CS-59	$Cu_{1.80}S$	500°C 3 days 300°C 7 days	dgt (5.7)+dj
CS-10	$Cu_{1.80}S$	600°C 7 days	dgt (6.0)
CS-71	$Cu_{1.82}S$	500°C 3 days 300°C 7 days	dgt (5.8)+anl+dj

(b) Starting from synthetic crystals

Sample No.	Composition	Starting material	Temperature and time	Results
CS-51a	$Cu_{1.75}S$	CS-51	300°C 4 days	cv, dgt (5.2), anl+dj
CS-51b	$Cu_{1.75}S$	CS-51a	300°C 4 days	cv, dgt (5.2), anl+dj
CS-51c	$Cu_{1.75}S$	CS-51	room temperature 6 months	dgt (5.0)
CS-59a	$Cu_{1.80}S$	CS-59	room temperature 24 hours	dgt (5.7)+anl+dj
CS-10a	$Cu_{1.80}S$	CS-10	room temperature 6 months	anl

[a] The results were obtained by microscope and X-ray single crystal techniques. Phases observed in one crystal are connected by + sign and those observed in only different crystals are by, sign. cv = covellite, dgt (N) = digenite-type phase with the *Na*-type structure, anl = anilite and dj = djurleite.

The range of the solid solution is apparently from $Cu_{1.765}S$ to $Cu_{1.79}S$ at room temperature. All digenite-type phases coexisting with covellite are of 5.2 *a*-type and those coexisting with djurleite are the 5.7 *a*-type. These values of N are in good agreement with those calculated from the displacements of the superstructure reflections in the powder patterns described by Roseboom. However, as described above, some crystals of $Cu_{1.75}S$ (CS-51) and $Cu_{1.80}S$ (CS-10) compositions indicate possible appearance of the 5 *a*-type and 6 *a*-type respectively.

Thus the cell edge of the digenite-type solid solution, Na, changes continuously with chemical composition from 5 *a* at $Cu_{1.75}S$ to 6 *a* at $Cu_{1.80}S$. The relation between the value of N and chemical composition is illustrated for synthetic specimens (Fig. 2).

ADDITIONAL EXPERIMENTS

In order to determine the phase relations of anilite and the digenite-type solid solution, additional experiments on synthetic and natural samples were made (Table 1(b)).

A crystal of $Cu_{1.80}S$ (CS-59), which was found to be a mixture of the 5.7 *a*-type and a small amount of djurleite soon after rapid cooling, changed to give the reflections from anilite at room temperature in one day after the cooling (CS-59a). At the same time the reflections from djurleite in the sample became stronger. This indicates that the 5.7 *a*-type decomposed to anilite and djurleite at room temperature. A crystal in the sample of $Cu_{1.80}S$ (CS-10) rapidly cooled from 600°C first gave the patterns of the 6 *a*-type soon after the cooling (Fig. 1c). By leaving the crystal at room temperature for six months (CS-10a), it completely changed to anilite without any observable amount of other phases. The anilite crystal became high digenite when heated at 80° ± 3°C and again changed to the 6 *a*-type on cooling to room temperature.

These experiments on crystals of $Cu_{1.80}S$ composition suggest the following changes:

$$\text{high digenite } (Cu_{1.80}S) \xrightarrow{<80°C} 6a\text{-type digenite } (Cu_{1.80}S)$$
$$\longrightarrow 5.7a\text{-type digenite } (Cu_{1.79}S) + \text{djurleite } (Cu_{1.97}S)$$
$$\longrightarrow \text{anilite } (Cu_{1.75}S) + \text{djurleite } (Cu_{1.97}S).$$

The sample $Cu_{1.75}S$ (CS-51), containing the crystal of the 5 *a*-type, was enclosed in an evacuated silica tube, heated at 305° ± 5°C for 105 hours and rapidly cooled to room temperature. The product (CS-51a) was a mixture of the 5.2 *a*-type, a small amount of covellite and anilite with a small amount of djurleite in an epitactic relation (Morimoto *et al.*, 1969). Repetition of the same experiment on CS-51a resulted in the same mixtures (CS-51b). A crystal of the 5 *a*-type (CS-51) was examined after

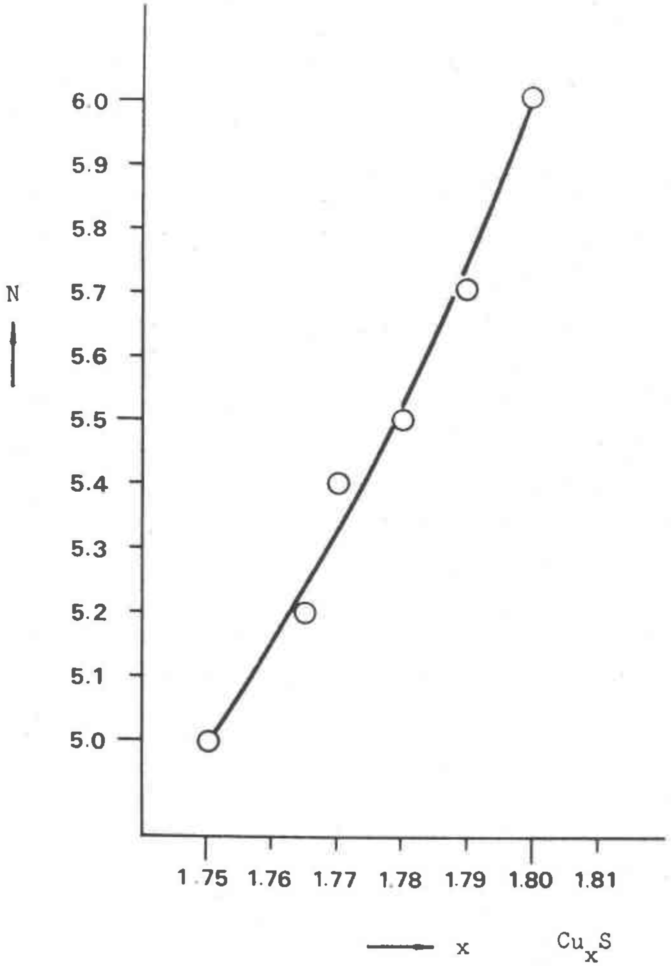


FIG. 2. Relations between chemical composition and $N(N=1/\delta t)$ for the digenite-type solid solution, whose cell edge is equal to N times that of the high-digenite subcell.

leaving in air at room temperature for six months (CS-51c). No change was observed. A crystal taken from the sample of $Cu_{1.75}S$ (CS-51a), consisting of anilite and a small amount of djurleite, was kept in air at 73° ± 3°C for one hour and slowly cooled to room temperature. The product was the 5.2 *a*-type without any observable amount of other phases. However, a natural crystal of anilite with a very small amount of djurleite was examined at 95° ± 3°C by the precession method. It gave the patterns of high digenite of the *a*-type. After cooling to room temperature, it was found to be the 5 a-type without any appreciable amount of other phases.

Interpretation of all the experimental results on samples of $Cu_{1.75}S$ composition, including anilite, is not straight forward. Although the 5 a-type and 5.2 a-type seem to stay permanently at room temperature without any change, they are considered to change to anilite or mixtures of anilite and djurleite respectively by slight heating. Thus the results can be summarized in the following way very much as for the specimens of $Cu_{1.80}S$ composition:

$$\begin{aligned}\text{high digenite } (Cu_{1.75}S) &\xrightarrow{<73°C} 5a\text{-type } (Cu_{1.75}S) \rightarrow 5.2a\text{-type } (Cu_{1.765}S) + \text{covellite } (CuS)\\ &\xrightarrow{\qquad} \text{anilite } (Cu_{1.75}S) + \text{djurleite } (Cu_{1.97}S) + \text{covellite } (CuS).\end{aligned}$$

The additional experiments on the synthetic crystals of $Cu_{1.75}S$ and $Cu_{1.80}S$ compositions indicate that the digenite-type solid solution is metastable and changes to mixtures of anilite and djurleite. The changes of the 5.7 a-type and 6 a-type to anilite and djurleite are much easier at room temperature than those of the 5 a-type and 5.2 a-type to anilite and a mixture of anilite and djurleite. This fact can be explained by easier exsolution of djurleite in the Cu-rich members than in Cu-poor members of the solid solution at room temperature.

DIGENITE PROBLEM

If anilite is stable at room temperature in the Cu-S system, we have to elucidate the stability of digenite in nature. The precession photograph of natural digenite (Morimoto *et al.*, 1969; Fig. 3) shows the pattern of the modified 5 a-type of cubic symmetry in which the superstructure reflections do not obey the extinction rules of the digenite-type solid solution. The superstructure reflections divide the repeat of the main reflections into five equal intervals along the $\langle 111 \rangle^*$ directions and give a cubic cell of $a = 27.90 \pm 0.01$ Å (Morimoto *et al.*, 1969). By heating at 80°C, digenite changed to high digenite of a-type. After cooling to room temperature, it changed to the 5 a-type which corresponds to the digenite-type solid solution of $Cu_{1.75}S$ composition, suggesting that the composition of digenite is close to $Cu_{1.75}S$. The crystal finally changed to the modified 5 a-type in a week at room temperature. Synthetic crystals of $Cu_{1.75}S$ composition with no iron, however, stayed as the 5 a-type or as a mixture of the 5.2 a-type and covellite at room temperature and never changed to the modified 5 a-type even in six months after cooling. The cell edge of the synthetic crystal is $a = 27.79 \pm 0.01$ Å, slightly smaller than that of digenite.

The electron-probe analysis of digenite, Leonard Mine, Butte, Montana was carried out by Dr. Y. Shimazaki. The result is Cu 78.0, Fe 1.1

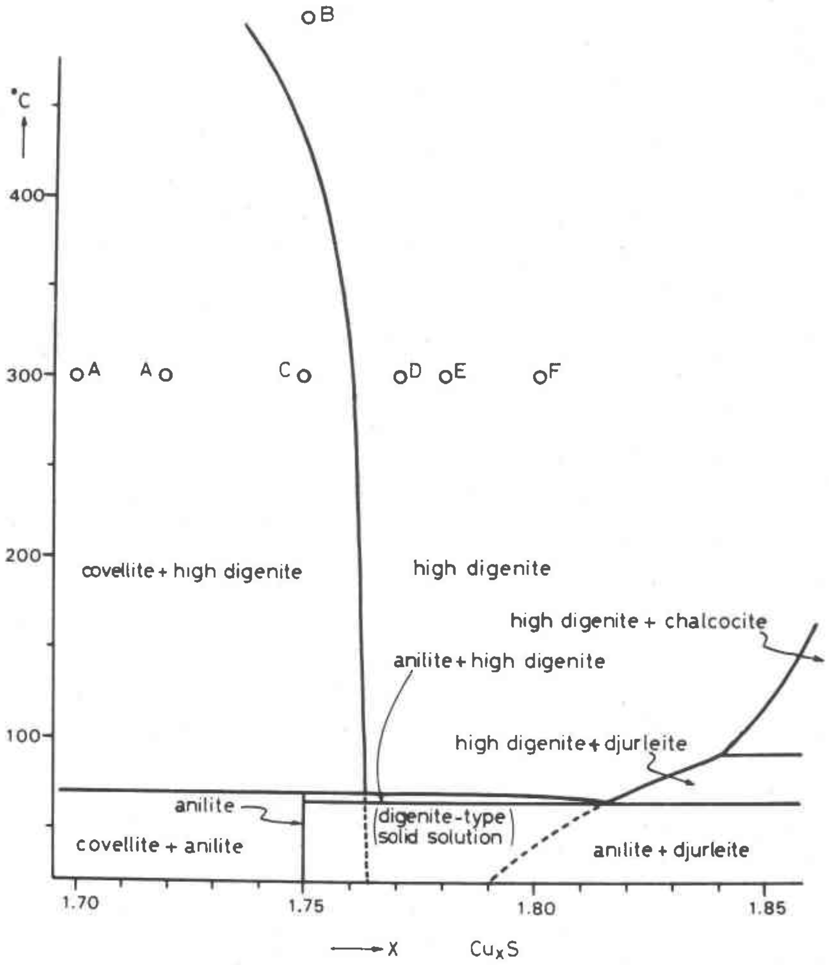


FIG. 3. Possible phase relations of the Cu-S system. The phase relations of high digenite above 90°C were taken from Roseboom (1966). The phase relations of specimens denoted by capital letters are explained in the text. Possible metastable phase relations are shown by broken lines.

and S 22.4 weight percent, giving the formula $Cu_{7.00}Fe_{0.12}S_{4.00}$. In order to make clear the role of iron in digenite, crystals were synthesized with the composition of $Cu_{6.90}Fe_{0.10}S_4$ and $Cu_{6.85}Fe_{0.15}S_4$ at 500°C. For both crystals, the 5 a-type first appeared after rapid cooling and gradually changed to the modified 5 a-type at room temperature which is the same as digenite. The cell edges of the modified 5 a-type are 27.90±0.05 Å in good agreement with that of digenite.

These results indicate that digenite is stable at room temperature only when it contains a small amount of iron. The stability field of digenite in the Cu-Fe-S system is now under investigation.

DISCUSSION

The conspicuous variations of the intensity maxima of the superstructure reflections with change of composition in the digenite-type solid solution are quite similar to those of "*c*"-type reflections observed in the nonintegral type of pyrrhotite (Morimoto and Nakazawa, 1968). These superstructure reflections are commonly observed in synthetic sulfides with solid solution ranges. However, none of the nonintegral types of the digenite type solid solution has ever been found as a mineral. This strongly supports the conclusion obtained by the synthetic experiments that the nonintegral types of the solid solution are metastable at room temperature and change to anilite and djurleite, both of which show the usual superstructures of the integral type (Morimoto and Nakazawa, 1968) and have stoichiometric chemical compositions.

On the basis of the synthesis and crystallographic studies of anilite, digenite and the digenite-type solid solution, probable phase relations of the Cu-S system at low temperatures are constructed (Fig. 3). In the phase diagram, the metastable digenite-type solid solution are entirely ignored and the stable field for anilite + djurleite is considered. The stability range of high digenite above 90°C is taken from Roseboom's diagram (1966). The field for anilite + high digenite may be extremely small, perhaps extending over only a fraction of a degree.

All the results of the experiments, some of which were apparently conflicting, were well explained on the basis of these phase relations, in view of the fact that reversals of all the reactions were not achieved. When the specimen *A* (Fig. 4, and CS-62 and CS-65 in Table 1) is quenched, the product is at first a mixture of covellite and the 5.2 *a*-type. The latter is considered to change finally to anilite and djurleite. When the specimen *B* is quenched, the 5 *a*-type is obtained. The specimen CS-51 is considered to correspond to this case though it was once annealed at 300°C after heating at 500°C. However, when the specimen consists of high digenite and covellite as *C* (CS-56 and CS-55), the quenched product is a mixture of the 5.2 *a*-type and covellite. The crystals of the 5.2 *a*-type in the quenched product of the specimen *C* occasionally change to stable phases at low temperature anilite and djurleite (CS-17). When the specimens *D* (CS-73) and *E* (CS-76) are quenched, they become the 5.4 *a*-type and 5.5 *a*-type respectively or mixtures of anilite and djurleite corresponding to the low temperature assemblage. When the specimen *F* (CS-10) is rapidly cooled, it becomes the 6 *a*-type, and further decomposes to a mixture of the 5.7 *a*-type and djurleite (CS-59). The 5.7 *a*-type finally becomes a mixture of anilite and djurleite (CS-59). The metastable solid solution of digenite-type is shown by broken lines in Fig. 3.

NATURAL OCCURRENCES

According to the phase relation (Fig. 3), anilite can have paragenetic relations with djurleite and covellite. In the specimens from the Ani Mine, anilite and djurleite are commonly found in association. Takeda *et al.* (1964, 1967) mentioned a digenite-like phase formerly designated as djurleite I by Sadanaga, Morimoto, and Ohmasa (1963) that occurs with djurleite in a specimen from Neudorf, Germany. The precession patterns of this crystal agree with those of anilite (Takeda, private communication, 1967). Clark and Sillitoe (private communication, 1969) found anilite associated with djurleite and covellite in Estrella Mine, Atacama Province, Chili.

It is not clear at present whether anilite can coexist with digenite. Only by the single crystal method can such coexistence be detected.

ACKNOWLEDGMENTS

We thank Dr. Y. Shimazaki, Geological Survey of Japan, for the electron-probe analysis of digenite. Professor J. D. H. Donnay, Dr. G. Donnay, Dr. G. Kullerud and Dr. Larry Taylor reviewed the manuscript and provided numerous suggestions for its improvement. Dr. A. H. Clark kindly supplied valuable information on the occurrence of anilite prior to publication.

Part of the expenses of this work was defrayed by a grant for scientific research from the Ministry of Education of the Japanese Government.

REFERENCES

DONNAY, G., J. D. H. DONNAY, AND G. KULLERUD (1958) Crystal and twin structure of digenite Cu_9S_5. *Amer. Mineral.* **43,** 230–242.

DJURLE, S. (1958) An x-ray study on the system Cu-S. *Acta Chem. Scand.* **12,** 1415–1426.

MOH, G. H. (1964) Blaubleibender covellite. *Carnegie Inst. Wash. Year Book* **63,** 208–209.

MORIMOTO, N., K. KOTO, AND Y. SHIMAZAKI (1969) Anilite, Cu_7S_5, a new mineral. *Amer. Mineral.* **54,** 1256–1258.

——— AND G. KULLERUD (1963) Polymorphism in digenite. *Amer. Mineral.* **48,** 110–123.

——— AND ——— (1966) Polymorphism on the Cu_5FeS_4-Cu_9S_5 join. *Z. Kristallogr.* **123,** 235–254.

——— AND H. NAKAZAWA (1968) Pyrrhotites, synthetics having two new superstructures. *Science* **161,** 577–579.

ROSEBOOM, E. H. (1966) An investigation of the system Cu-S and some natural copper sulfides between 25° and 700°C. *Econ. Geol.* **61,** 641–672.

SADANAGA, R., N. MORIMOTO, AND M. OHMASA (1963) X-ray studies of djurleite [*abstr.*] *Ann. Meet. Mineral. Soc. Jap.* [In Japanese].

TAKEDA, H. AND J. D. H. DONNAY (1964) Twinning interpretation of superlattice reflections of copper sulfides [*abstr.*] *Prog. Joint Meet. Mineral. Soc. Amer. Crystallogr. Ass.*

———, ———, E. H. RCSEBOOM, AND D. E. APPELMAN (1967) The crystallography of djurleite, $Cu_{1.97}S$. *Z, Kristallogr.* **125,** 404–413.

Manuscript received, June 5, 1969; accepted for publication, October 3, 1969.