

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

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ABSTRACT

Anilite, digenite and synthetic samples of the composition range $\text{Cu}_{1.76}\text{S}-\text{Cu}_{1.82}\text{S}$ have been studied by the X-ray diffraction and microscopy. At room temperature, the stable phases in the range of composition studied are djurleite ($\text{Cu}_{1.97}\text{S}$), anilite ($\text{Cu}_{1.76}\text{S}$) and covellite (CuS). Above $70^\circ \pm 3^\circ\text{C}$, anilite decomposes to high digenite and covellite.

The digenite-type solid solution usually appears in synthetic experiments with composition between $\text{Cu}_{1.765}\text{S}$ and $\text{Cu}_{1.79}\text{S}$ at room temperature as indicated by Roseboom (1966), but its composition range occasionally extends from $\text{Cu}_{1.76}\text{S}$ to $\text{Cu}_{1.80}\text{S}$. 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 ($\text{Cu}_{1.97}\text{S}$), digenite-type solid solution¹ and covellite (CuS). Roseboom (1966) indicated that the digenite-type solid solution is stable in the composition range $\text{Cu}_{1.765}\text{S}-\text{Cu}_{1.79}\text{S}$ at room temperature and that the Cu-poor limit is not affected by temperature, while the Cu-rich limit changes to $\text{Cu}_{1.83}\text{S}$ 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 $a=5.57 \text{ \AA}$ 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 \AA . He observed, however, anomalous displacements of weak lines with change of composition, which he described as follows:

... digenite of $\text{Cu}_{1.765}\text{S}$ 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 $\text{Cu}_{1.75}\text{S}$ 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 $\text{Cu}_{1.75}\text{S}$ (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 $\text{Cu}_{1.70}\text{S}-\text{Cu}_{1.83}\text{S}$. 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 $0.01\sim 0.3$ mm in size, which were examined by the X-ray powder and precession methods using $\text{CuK}\alpha$ radiation (1.5418 \AA). 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 $\text{Cu}_{1.70}\text{S}$ - $\text{Cu}_{1.82}\text{S}$ (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 $\text{Cu}_{1.72}\text{S}$ (CS-62 and CS-65), obtained by rapid cooling from 300°C , were found to be a mixture of the digenite-type phase of $\text{Cu}_{1.765}\text{S}$ composition, which was the most Cu-poor member in the solid solution by Roseboom (1966), and covellite. The samples of $\text{Cu}_{1.75}\text{S}$ 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 ($\text{Cu}_{1.765}\text{S}$) 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 $\text{Cu}_{1.75}\text{S}$ composition will be discussed later. Synthetic samples of $\text{Cu}_{1.77}\text{S}$ and $\text{Cu}_{1.78}\text{S}$ compositions were found to be the digenite-type phases without other phases or to be a mixture of anilite and djurleite in an epitaxial relation (CS-73 and CS-76). When the copper content was more than $\text{Cu}_{1.80}\text{S}$, the samples became a mixture of the digenite-type phase of $\text{Cu}_{1.79}\text{S}$ composition, which was the most Cu-rich member in the solid solution by Roseboom (1966), and djurleite. One crystal from the sample of $\text{Cu}_{1.80}\text{S}$ (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 compositions $\text{Cu}_{1.75}\text{S}$ (CS-51), $\text{Cu}_{1.78}\text{S}$ (CS-76) and $\text{Cu}_{1.80}\text{S}$ (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 $a \sim 5.57 \text{ \AA}$ (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 $\langle 111 \rangle^*$ direction, resulting in a supercell of cubic symmetry with $a = 27.79 \text{ \AA}$. 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 $\langle 111 \rangle^*$ 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 $(h \pm n\delta l, k \pm n\delta l, l \pm n\delta l)$, where h, k and l are integers and refer to the high-digenite subcell, n is an integer (usually one, two or three) and δl represents a nonintegral positive number. If we regard the superstructure reflections as satellite reflections of the n th order of a main reflection (h, k, l) , δl 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 δl are, therefore, $1/5$, $1/5.5$ and $1/6$ for the digenite-type phases of $\text{Cu}_{1.75}\text{S}$, $\text{Cu}_{1.78}\text{S}$ and $\text{Cu}_{1.80}\text{S}$ 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 $1/\delta l$. 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.

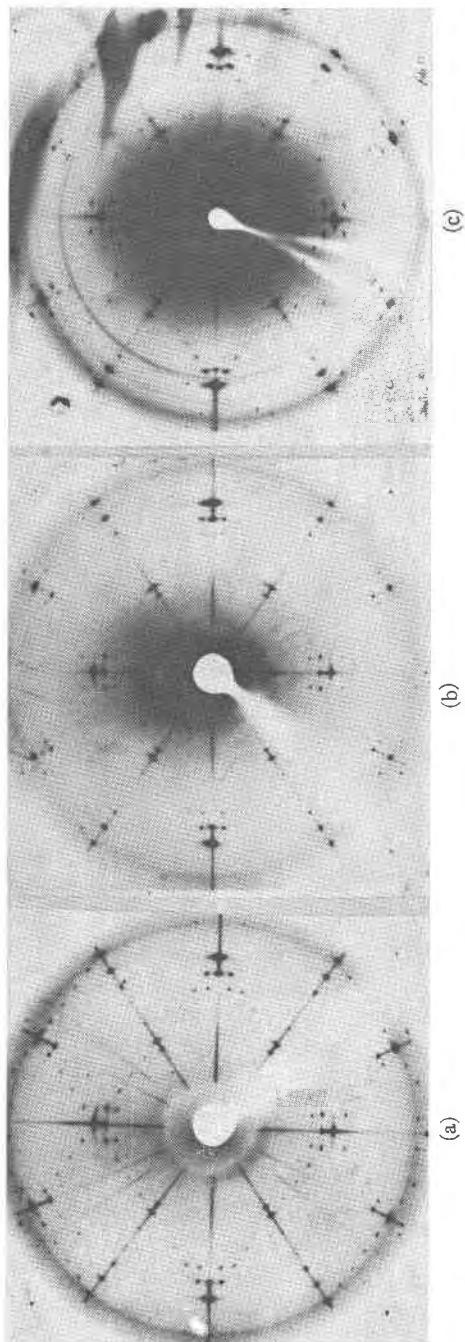


FIG. 1. Precession photographs $(1\bar{1}0)_0^*$ of synthetic digenite-type phases with compositions $\text{Cu}_{1.75}\text{S}$ (CS-51) (a), $\text{Cu}_{1.75}\text{S}$ (CS-76) (b), and $\text{Cu}_{1.80}\text{S}$ (CS-10) (c).

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

(a) Starting from mixtures of elements				
Sample No.	Composition	Temperature and time		Result
CS-62	$\text{Cu}_{1.70}\text{S}$	500°C 3 days		cv, dgt (5.2)
		300°C 7 days		
CS-65	$\text{Cu}_{1.72}\text{S}$	500°C 3 days		cv, dgt (5.2)
		300°C 7 days		
CS-17	$\text{Cu}_{1.76}\text{S}$	500°C 3 days		cv, anl+dj
		300°C 7 days		
CS-49	$\text{Cu}_{1.75}\text{S}$	500°C 3 days		cv, dgt (5.2), anl+dj
		300°C 7 days		
CS-51	$\text{Cu}_{1.75}\text{S}$	500°C 3 days		dgt (5.0)
		300°C 7 days		
CS-55	$\text{Cu}_{1.76}\text{S}$	500°C 3 days		cv, dgt (5.2)
		300°C 7 days		
CS-56	$\text{Cu}_{1.75}\text{S}$	500°C 3 days		cv, dgt (5.2)
		300°C 7 days		
CS-73	$\text{Cu}_{1.77}\text{S}$	500°C 3 days		dgt (5.4), anl+dj
		300°C 7 days		
CS-76	$\text{Cu}_{1.76}\text{S}$	500°C 3 days		dgt (5.5), anl+dj
		300°C 7 days		
CS-59	$\text{Cu}_{1.80}\text{S}$	500°C 3 days		dgt (5.7)+dj
		300°C 7 days		
CS-10	$\text{Cu}_{1.80}\text{S}$	600°C 7 days		dgt (6.0)
CS-71	$\text{Cu}_{1.82}\text{S}$	500°C 3 days		dgt (5.8)+anl+dj
		300°C 7 days		

(b) Starting from synthetic crystals

Sample No.	Composition	Starting material	Temperature and time	Results
CS-51a	$\text{Cu}_{1.75}\text{S}$	CS-51	300°C 4 days	cv, dgt (5.2), anl+dj
CS-51b	$\text{Cu}_{1.75}\text{S}$	CS-51a	300°C 4 days	cv, dgt (5.2), anl+dj
CS-51c	$\text{Cu}_{1.75}\text{S}$	CS-51	room temperature 6 months	dgt (5.0)
CS-59a	$\text{Cu}_{1.80}\text{S}$	CS-59	room temperature 24 hours	dgt (5.7)+anl+dj
CS-10a	$\text{Cu}_{1.80}\text{S}$	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 *N* α -type structure, anl=anilite and dj=djurleite.

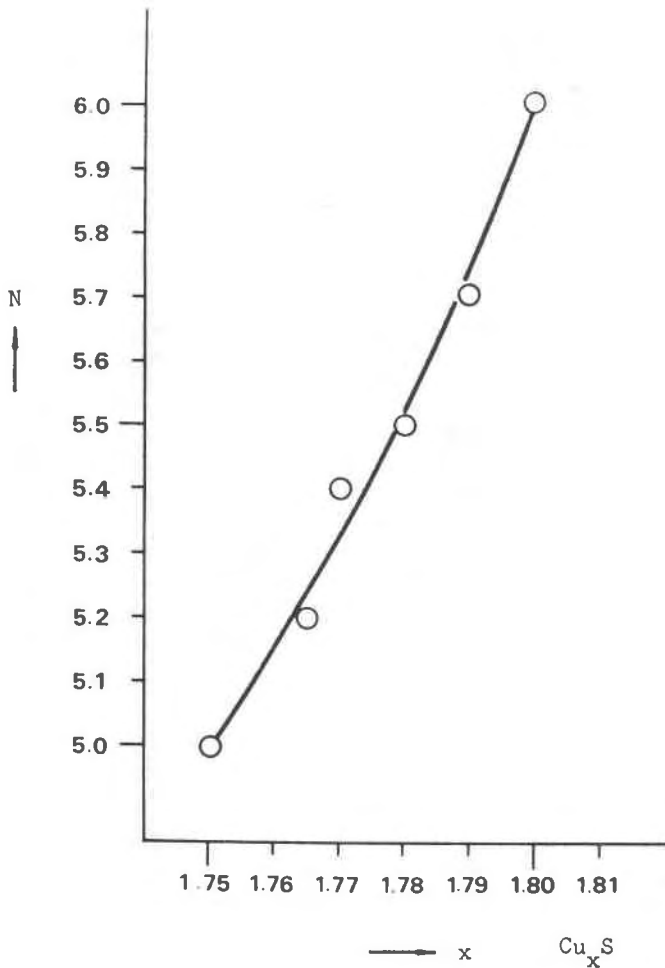


FIG. 2. Relations between chemical composition and $N(N=1/\delta t)$ for the digenite-type solid solution, whose cell edge is equal to N times that of the high-digenite subcell.

leaving in air at room temperature for six months (CS-51c). No change was observed. A crystal taken from the sample of $\text{Cu}_{1.75}\text{S}$ (CS-51a), consisting of anilite and a small amount of djurleite, was kept in air at $73^\circ \pm 3^\circ\text{C}$ 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 $95^\circ \pm 3^\circ\text{C}$ by the precession method. It gave the patterns of high digenite of the a -type. After cooling to room tem-

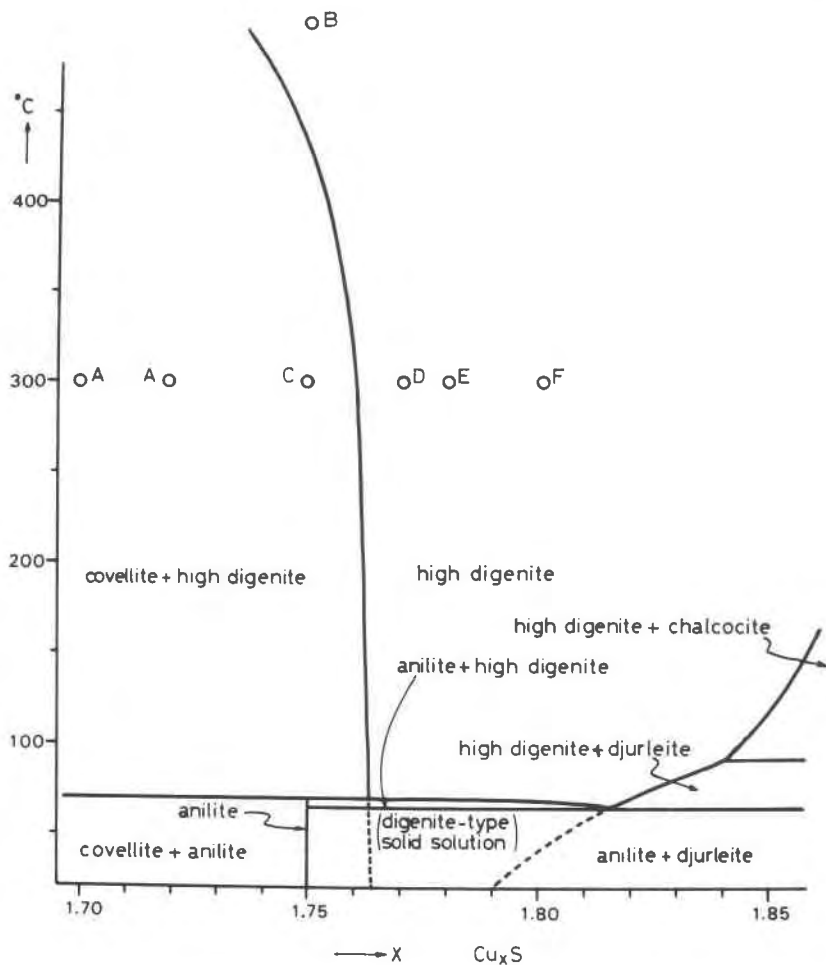


Fig. 3. Possible phase relations of the Cu-S system. The phase relations of high digenite above 90°C were taken from Roseboom (1966). The phase relations of specimens denoted by capital letters are explained in the text. Possible metastable phase relations are shown by broken lines.

and S 22.4 weight percent, giving the formula $\text{Cu}_{7.00}\text{Fe}_{0.12}\text{S}_{4.00}$. In order to make clear the role of iron in digenite, crystals were synthesized with the composition of $\text{Cu}_{6.90}\text{Fe}_{0.10}\text{S}_4$ and $\text{Cu}_{6.85}\text{Fe}_{0.15}\text{S}_4$ 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 $27.90 \pm 0.05 \text{ \AA}$ 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.

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