ANILITE, Cu7S4, A NEW MINERAL

Nobuo Morimoto and Kichiro Koto, *Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka*

AND

Yoshihiko Shimazaki, *Geological Survey of Japan, Kawata-cho, Shinjuku, Tokyo*

Abstract

Anilite, a new mineral from the Ani Mine, Akita, Japan, has an extremely narrow range of composition near Cu_7S_4, confirmed by synthesis. It crystallizes in $Pnma$, with $a=7.89$, $b=7.84$ and $c=11.01$ Å, all $\pm 0.2\%$, $Z=4$, $\rho=5.68$ g/cm³. Anilite can easily change by grinding to the metastable digenite-type phase giving the strongest lines: 3.20(40)(555), 2.78(40)(10.0.0) and 1.965(100)(10.10.0). The powder pattern of synthetic Cu_7S_4 (without grinding) gave the strong lines: 3.20(57)(202, 022), 2.77(65)(220), 2.16(39)(214, 124), 1.956(100)(040, 224) and 1.677Å(35)(422, 242), whose intensities agree with those calculated from the observed single-crystal intensities. Anilite is associated with djurleite. The twinning of anilite is governed by the pseudo-cubic subcell $(\frac{1}{2}\frac{1}{2}0/\frac{1}{2}\frac{1}{2}0/00\frac{1}{2})$ of sulfur close packing. In epitactic intergrowths, anilite and djurleite share a close packed plane of sulfur atoms.

Introduction

Since the first description of djurleite (Morimoto, 1962; Roseboom, 1962), many studies have been made of the compounds in the Cu-S system. Sadanaga, Morimoto, and Ohmasa (1963) suggested that djurleite might be a mixture of mutually oriented crystals of two different phases: "djurleite I", similar to digenite, and "djurleite II", similar to chalcocite. They determined the cell dimensions of the phases on crystals from the Ani Mine, Akita, Japan, by the single-crystal X-ray method. Sadanaga and Ohmasa (priv. commun., 1963) found, associated with chalcocite in a specimen from St. Ives, Cornwall, an unidentified orthorhombic phase for which they determined the cell dimensions and space group. Takeda and Donnay (1964) also described a copper sulfide mineral from Neudorf, Germany, with the same cell dimensions and space group that Sadanaga and Ohmasa reported for their unidentified orthorhombic phase.

In order to elucidate the relation between this unidentified phase and the material from the Ani Mine, the latter mineral has been studied in detail. Experiments on synthetic compounds of the Cu-S system have also been carried out in order to confirm the results obtained with the natural material.

While our study was in progress, Roseboom (1966) and Takeda *et al.*

(1967) studied djurleite from various localities and concluded that djurleite is a valid species, different from chalcocite and digenite in crystallographic properties and composition. Their X-ray studies have shown the unidentified species studied by Sadanaga and Ohmasa (1963) and Takeda and Donnay (1964) to be djurleite.

The present paper summarizes the results of the study on the material from the Ani Mine, in the course of which a new copper sulfide mineral, Cu_7S_4, was discovered. The mineral is named anilite after the Ani Mine, Akita, Japan, where the first specimen was discovered. This name has been submitted to and approved by the Commission on New Mineral Names of the International Mineralogical Association. The material from the Ani Mine has now been shown to consist of two copper sulfide minerals: anilite and djurleite, structurally similar to digenite and chalcocite, respectively.

MATERIALS

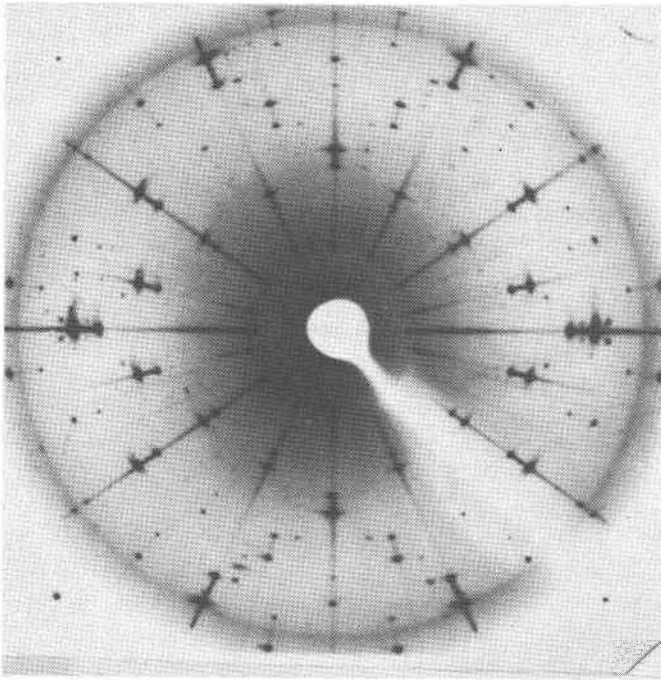Anilite is similar to chalcocite in appearance and is found as prismatic

FIG. 1. Precession photograph $(100)_0^*$ of anilite with a small amount of djurleite, from Ani Mine, Akita, Japan.
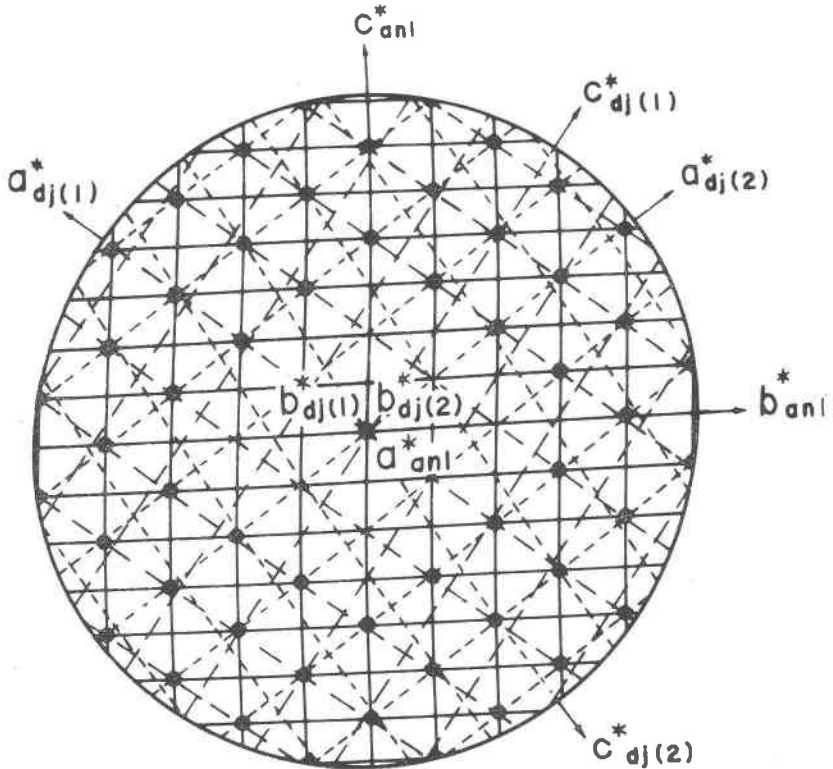
FIG. 2. Reciprocal nets of anilite and djurleite in Fig. 1. The net for
djurleite is drawn with the translations 4a* and 2c* for simplicity.

or platy crystals up to 5 mm in size in drusy parts of the quartz vein of the
Ani Mine.

The existence of at least two phases in the samples was confirmed by
the X-ray precession method. They are djurleite (Morimoto, 1962;
Roseboom, 1962) and anilite. Although djurleite was occasionally found
as single crystals, most specimens were mixtures of the two phases. A
precession photograph of the mixture (Fig. 1) and the relationship be-
tween the reciprocal lattices of the two phases are given (Fig. 2).

Attempts to isolate a single crystal of anilite failed, as was to be ex-
pected from the fine intergrowth with djurleite. In some of the Ani
specimens, however, anilite was the dominant constituent, with a very
small amount of djurleite.

A few specimens, which were confirmed to be mostly anilite with a
small amount of djurleite by the X-ray method, were mounted in plastic

cement and polished for microscopic observation and electron-probe analysis. The polished specimens are homogeneous and isotropic like digenite. As will be explained later, the mixture of anilite and djurleite is considered to have transformed to a homogeneous digenite-like phase at the surface in the process of polishing. This is also confirmed by the result of electron-probe analysis as described later.

The color of the Ani specimen is bluish gray and its luster is metallic. The streak is black. The hardness (Mohs) is about 3. No cleavage is observed, but the crystal is sectile. The calculated specific gravity is 5.68. The type material is preserved in the Sakurai Museum, Tokyo.

CHEMISTRY

Electron-probe analysis. In order to determine the chemical composition of anilite, two crystals from the Ani Mine were examined by electron-probe microanalyser. The crystals were first examined by the X-ray single-crystal method before the electron-probe analysis and were found to be anilite with a small amount of djurleite, though the amount of djurleite relative to anilite was not estimated. For comparison, synthetic samples of $Cu_{1.77}S$ composition, consisting of anilite and a very small amount of djurleite, were also analysed. All specimens, mounted in plastic cement and polished, were found to be homogeneous microscopically.

The samples were coated with carbon and X-ray excitation was achieved by 25 KeV electrons. As the material is thermally sensitive, an electron beam with diameter of $1\mu m$ damaged the surface severely and thus it was widened to approximately $20 \mu m$ which produced satisfactory results. Since the polishing necessary for the analysis produced homogeneous material, the larger beam does not affect the analysis and it was confirmed by measurements at different points of the specimens and by fine profile with narrower beams. The measured intensities were corrected for dead time, background, and for mass absorption by Philbert's method and the atomic numbers effects, by Poole and Thomas's method. Chalcopyrite of known composition was used for standard.

The chemical compositions of the natural samples (Table 1) correspond to mixtures of anilite and djurleite in different ratios. The absence of elements other than Cu and S was confirmed for Mg-U by electron probe. The analysis of the synthetic material resulted in exactly $Cu_{1.77}S$. Because the chemical composition of djurleite is $Cu_{1.97}S$ (Roseboom, 1966),

TABLE 1. ELECTRON-PROBE ANALYSIS OF ANILITE

	Cu	S	Total (wt %)	Composition
1	79.2	21.7	100.9	$Cu_{1.84}S$
2	80.1	22.7	102.8	$Cu_{1.78}S$
3	77.8	22.1	99.9	$Cu_{1.77}S$
4	77.6	22.4	100.0	$Cu_{1.75}S$

1 and 2. Natural specimens.
3. Synthetic specimen of $Cu_{1.77}S$ composition.
4. Theoretical values for Cu_7S_4.
1, 2 and 3. Analyst: Y. Shimazaki.

we came to the conclusion that the composition of anilite is close to $Cu_{1.75}$ S, which was later confirmed by the synthetic work and the crystal structure determination.

Synthesis. In order to establish the chemical composition of anilite accurately, experiments on the synthesis of anilite were carried out. Because the composition of anilite is considered close to $Cu_{1.75}S$, materials with compositions between $Cu_{1.70}S$ and $Cu_{1.82}S$ were synthesized by the dry method starting from mixtures of copper and sulfur.

The X-ray powder method and the reflecting microscope were not suitable for identifying the phase in the synthetic samples, because anilite changed to a digenite-like phase by grinding as will be described later. Only covellite was confirmed by the microscope. In order to confirm the existing phases in the synthetic products, several single crystals were picked from the product of each run and examined by X rays.

Synthetic samples richer in sulfur than $Cu_{1.72}S$ obtained by rapid cooling from 300°C were found to be mixtures of covellite and the digenite-type phase[1] of $Cu_{1.765}S$ composition which was described by Roseboom (1966) as the Cu-poor limit of the digenite-type solid solution. For the samples of $Cu_{1.75}S$ composition rapidly cooled from 300°C, the digenite-type phase of $Cu_{1.75}S$ composition or the mixture of the digenite-type phase of $Cu_{1.765}S$ and covellite was obtained in most cases, but occasionally anilite was found with small amounts djurleite and covellite. Most crystals with the composition $Cu_{1.77}S$-$Cu_{1.78}S$, rapidly cooled from 300°C, were found to be the digenite-type phase but some crystals were found to be mixtures of anilite and djurleite. Crystals of $Cu_{1.80}S$ composition, were mixtures of the digenite-type phase of $Cu_{1.79}S$, the Cu-rich limit of the solid solution according to Roseboom (1966), and djurleite. The crystals changed to the mixture of the digenite-type phase of $Cu_{1.79}S$, anilite and djurleite in one day at room temperature after rapid cooling, indicating the decomposition of the digenite-type phase to anilite and djurleite.

All the experiments indicate that the digenite-type phase in the composition range between $Cu_{1.765}S$ and $Cu_{1.79}S$ is chemically equivalent to mixtures of anilite and djurleite. Coexistence of three phases (anilite, covellite, and djurleite) was found only in the samples of $Cu_{1.75}S$ composition. In samples consisting of anilite and djurleite, the amount of anilite is greater for those closer to the composition $Cu_{1.75}S$. Thus we can consider that the composition of anilite is $Cu_{1.75}S$ or Cu_7S_4, though we have not succeeded in obtaining anilite as a single phase.

CRYSTALLOGRAPHY

Single-crystal study. The cell dimensions of anilite, obtained by the precession method, are $a = 7.89$, $b = 7.84$ and $c = 11.01$ Å, all ± 0.2 percent. There are $4Cu_7S_4$ per cell. The cell volume is 681.1 Å^3. The calculated density is 5.68 g/cm^3 for $Z = 4$. The diffraction aspect is $Pn*a$; space group *Pnma* was confirmed by structure determination (Koto & Morimoto, 1968). If the number of Cu atoms in the unit cell is reduced from 28 to 27, the corresponding formula becomes $Cu_{1.69}S$; if it is increased to 29, the

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[1] This corresponds to the "digenite solid solution" described by Roseboom (1966). We call it *digenite-type solid solution* or simply *digenite-type phase* in this paper, because this solid solution is different from natural digenite (Morimoto & Koto, in preparation).
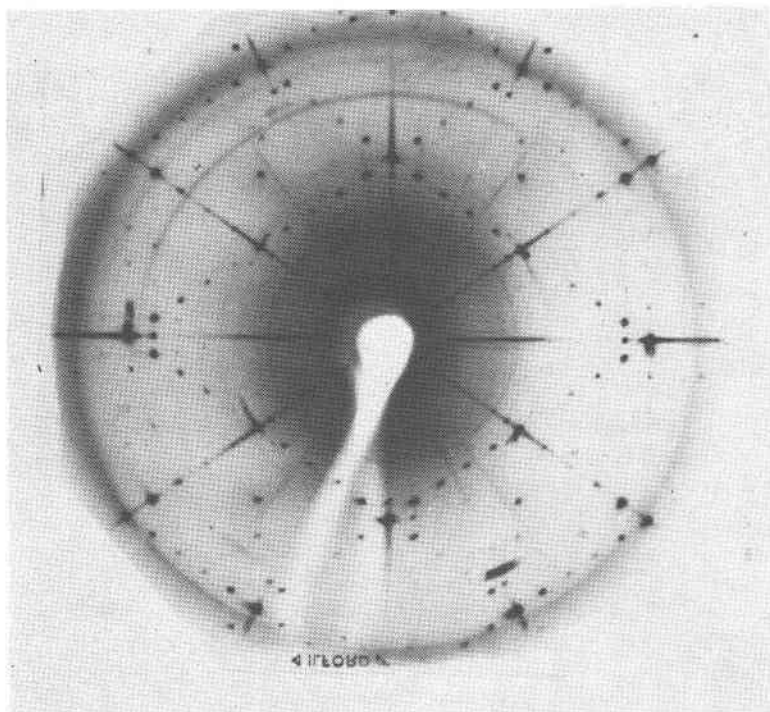
FIG. 3. Precession photograph $(1\bar{1}0)_0{}^*$ of digenite, from Leonard
Mine, Butte, Montana.

formula is $Cu_{1.81}S$. Both formulae are outside the range of possible composition found in our experiments.

From the pseudotetragonal cell of anilite, a pseudo cubic subcell, with cell edge of $\sim$5.5 Å, can be derived by the transformation matrix $\frac{1}{2}\frac{1}{2}0/\frac{1}{2}\frac{1}{2}0/00\frac{1}{2}$. This cubic cell is that of the cubic closest packing of sulfur atoms with metal atoms in their interstices in the high-temperature form of bornite-digenite solid solution (Morimoto and Kullerud, 1963, 1966). The single crystal pattern of anilite (Fig. 1) is, however, quite different from that of natural digenite from Leonard Mine, Butte, Montana (Fig. 3) (Morimoto and Kullerud, 1963). The pattern of the digenite-type phase is very similar to but definitely different from that of digenite (Morimoto and Koto, in preparation). The whole-rotation photograph of a synthetic specimen of anilite around the b axis is compared with one of digenite around [110] (Fig. 4(a) and (c)). The difference between them is clear.

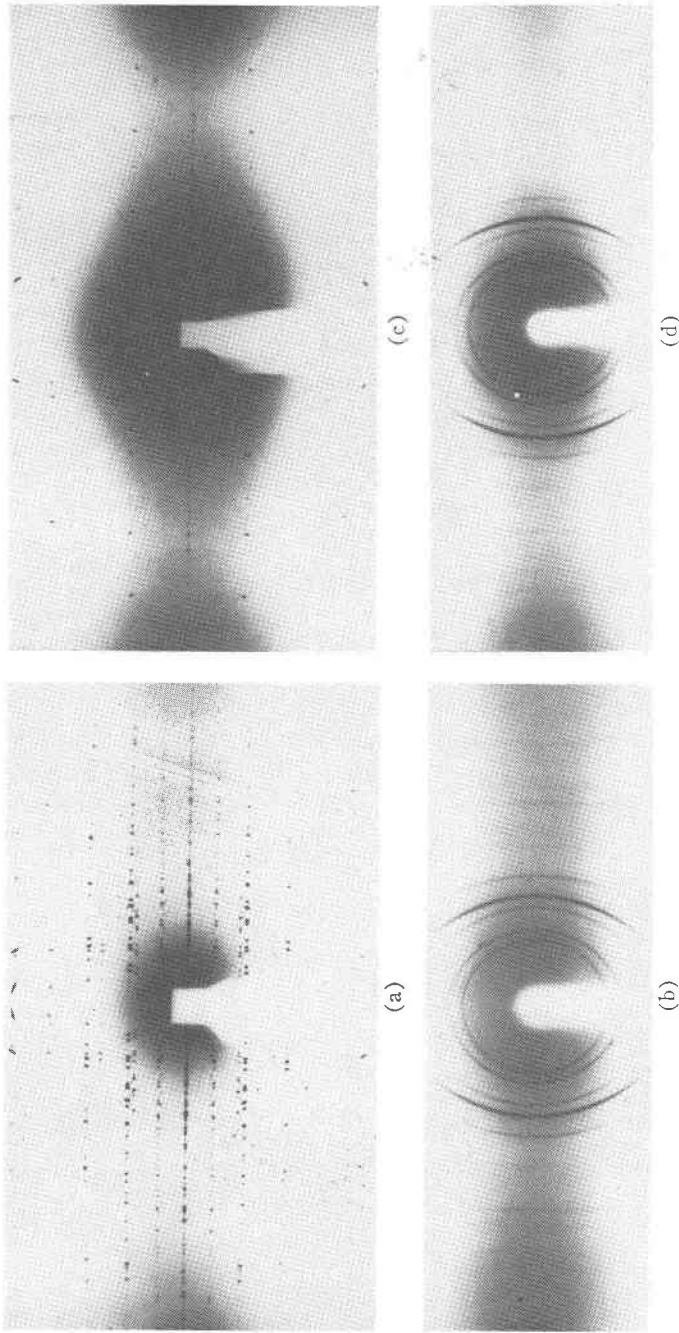Single crystals synthesized at $Cu_{1.75}S$ composition gave the pattern of

FIG. 4. Whole-rotation photograph of synthetic anilite around the b axis (a) and that of digenite around the corresponding direction [110] (c). Powder patterns of synthetic anilite (b) and digenite (d). The specimens for powder patterns were obtained by grinding the single crystals used for (a) and (c).

anilite with very weak reflections of djurleite. Synthetic and natural crystals of anilite have the same cell dimensions.

A natural crystal of anilite with a very small amount of djurleite was examined at $73 \pm 3°C$ by the precession method. It gave the patterns of the high digenite of type a (Morimoto and Kullerud, 1966). After cooling to room temperature, it was found to be the digenite-type phase.

Powder crystal study. Because the single-crystal patterns of anilite are very different from those of digenite, some appreciable difference was expected between their powder patterns. However, the powder patterns of anilite and of the corresponding synthetic compound, both of which always contain a small amount of djurleite, were essentially the same as those of digenite. The powder pattern of a synthetic specimen, which gave the single-crystal patterns of anilite before grinding, was very similar to that of digenite, though the superstructure lines were not confirmed [Fig. 4(b) and (d)].

In order to obtain the powder pattern of anilite, the synthetic sample of $Cu_{1.75}S$ composition was used on the diffractometer *without grinding*. Because the sample consisted of small crystals as grown which were not fine enough for the diffractometer, the line intensities varied slightly depending on sample preparation. The three patterns obtained from three different preparations of the same sample [Fig. 5(b)–1, 2 and 3], are compared with the chart obtained from the single crystal data [Fig. 5(a)]. The agreement is good. The observed d are compared with the calculated values in Table 2, where the observed intensities were estimated by averaging those from three patterns [Fig. 5(b)–1, 2 and 3]. The strong lines are: 3.20 Å (57) (202, 022), 2.77 Å (65) (220), 2.16 Å (39) (214, 124), 1.956 Å(100) (040, 224) and 1.677 Å (35) (422, 242).

The powder patterns from slightly ground (Fig. 5(c)) and thoroughly ground (Fig. 5 d) samples illustrate the change from anilite to the digenite-type phase due to grinding. The pattern for the well ground sample gives $a = 5.558$ Å for the subcell. The observed d for digenite and the digenite-type phase obtained by grinding synthetic Cu_7S_4 are given for comparison (Table 2). The remarkable effect of grinding explains why anilite has not been recognized earlier in spite of its common occurrence in synthetic experiments.

Twinning and Epitaxy

Most specimens from Ani are mixtures of two phases, anilite and djurleite. The two phases are intergrown in a definite orientation or in epitactic relation. Each phase is in most cases in twin relation. The twin law of anilite and the epitaxy between anilite and djurleite will be explained.
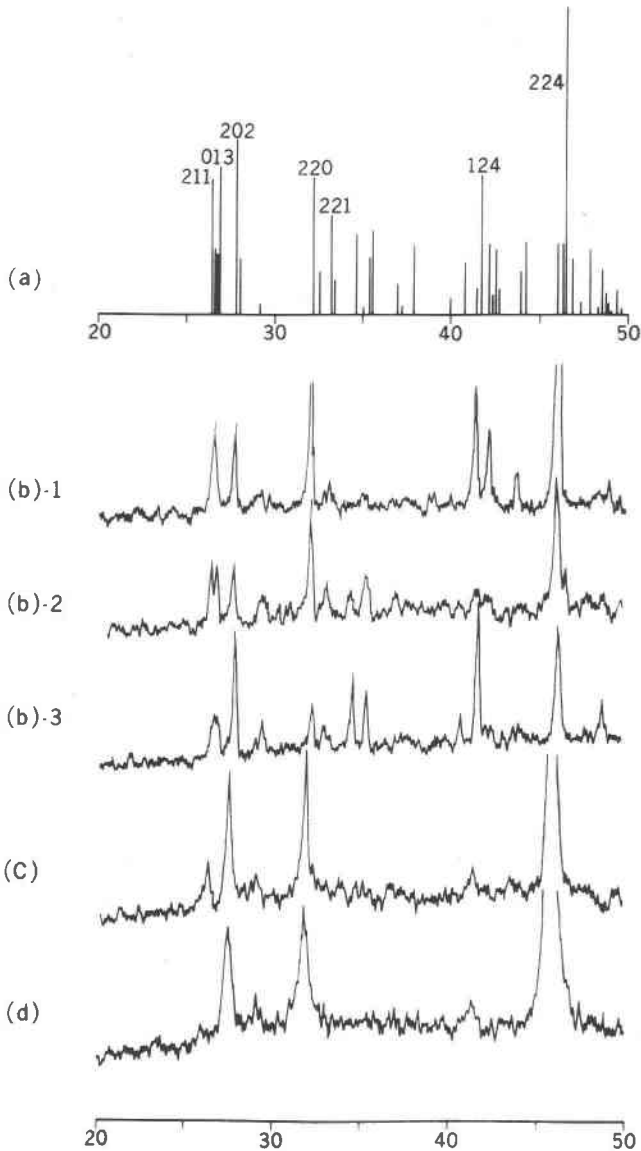
Fɪɢ. 5. Powder patterns of anilite. All patterns were taken in CuKα radiation (Ni filter). (a) Chart for powder reflections of anilite. Intensities and 2θ are calculated from the single-crystal data of anilite. (b)-1, 2 and 3. Obtained from three different preparations of the same specimen. Synthetic Cu_7S_4 was used as grown without grinding. (c) Obtained from the specimen used for (b) after slight grinding. (d) Obtained from the specimen used for (c) after well grinding.

TABLE 2. X-RAY POWDER DATA FOR ANILITE, DIGENITE, AND
DIGENITE-TYPE PHASE OF Cu_7S_4

Cu₇S₄[a]				Digenite[b]			Digenite-type phase[c]			
hkl	d(calc)	d(obs)	I(obs)	hkl	d	I	hkl	d(calc)	d(obs)	I
211	3.36	3.36	20							
121	3.35									
103	3.33	3.32	17							
013	3.32									
202	3.21	3.20	57	555	3.21	40	111	3.21	3.20	37
022	3.19									
				119	3.05	10				
220	2.78	2.77	65	0.0.10	2.79	40	002	2.78	2.78	40
004	2.75	2.75	6							
221	2.70	2.69	14							
104	2.60	2.59	29							
031	2.54									
213	2.54	2.54	31	1.1.11	2.53	5				
123	2.54									
302	2.37	2.39	10	4.4.10	2.40	5				
214	2.17	2.16	39	199	2.17	10				
124	2.17									
321	2.14									
303	2.14	2.13	15							
231	2.14									
313	2.06	2.05	5							
133	2.06									
040	1.960	1.956	100	0.10.10	1.973	100	022	1.965	1.965	100
224	1.956									
323	1.877									
233	1.873	1.873	10							
215	1.868									
314	1.848	1.847	3							
				999	1.781	5				
422	1.678	1.677	35	5.5.15	1.686	30				
242	1.672									

[a] Synthetic Cu_7S_4. Intensities were obtained by averaging those from three different preparations of the same sample as grown.

[b] Digenite, Leonard Mine, Butte, Montana. XRDF Card 9-64.

[c] Obtained by grinding synthetic Cu_7S_4. The d were calculated for $a = 5.558$ Å.

Twinning of anilite. The exact dimensions of the subcell are $a' = b' = 5.56$, $c' = 5.51$ Å and $\gamma' = 2 \arctan (a/b) = 90° 22'$. This subcell suggests that anilite may have a digenite-like structure, with cubic close packing of sulfur atoms. This was later confirmed by the structure determination (Koto and Morimoto, 1968).
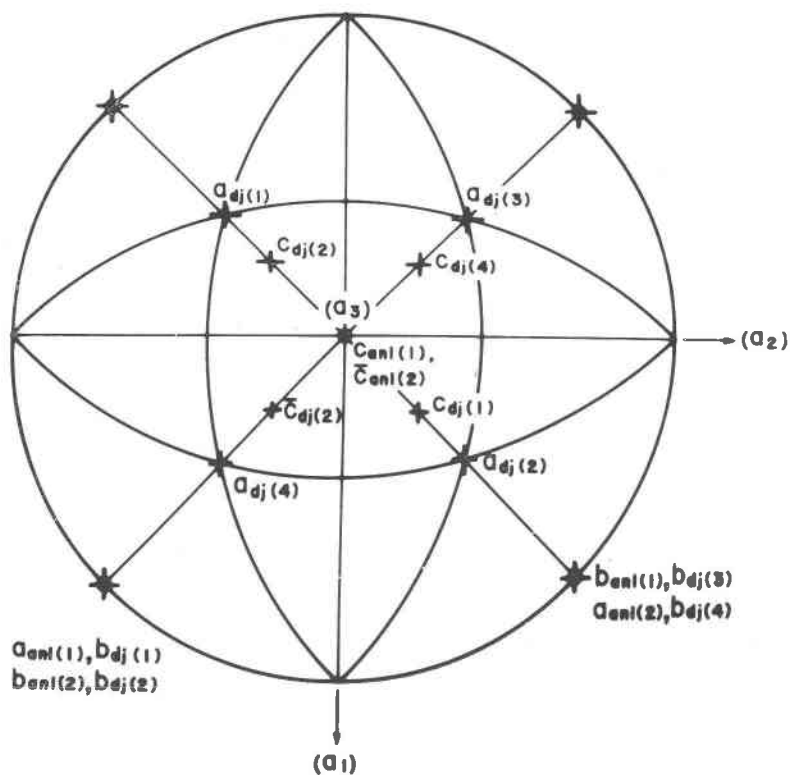
FIG. 6. Stereogram of the twinning and epitaxy of anilite and djurleite in the Ani specimen. The orientations of a_1, a_2 and a_3 indicate the cubic axes of the face-centered closest packing of sulfur atoms. Anilite 1 (anl(1)) and 2 (anl(2)) are in twin relation. Djurleite 1 (dj(1)) and 2 (dj(2)) are in epitactic relation with anilite 1, and djurleite 3 (dj(3)) and 4 (dj(4)) are in the same relation with anilite 2.

The possible twin operations are all the "cubic" symmetry operations of this subcell that do not rigorously exist in the original orthorhombic symmetry. In such twins, which G. Friedel called *macles voisines* or "neighboring twin" (Donnay, 1952), the possible twinned orientations do not differ much and are difficult to distinguish from one another because the translations along the pseudocubic axes are so nearly equal.

Observation shows that anilite really twins in this way and that the relative volumes of individual crystals in the twin are different from specimen to specimen. Most synthetic anilite samples also show this kind of twinning.

Epitaxy of anilite and djurleite. Anilite has the cubic closest packing of sulfur atoms and djurleite has the hexagonal closest packing (Takeda *et al.*, 1967). Therefore, the epitaxy of these phases is likely to take place in such a way that they share their closest-packed sulfur plane. The epitaxy observed in natural materials supports this relation (Fig. 1).

Specimens in which the epitaxy of anilite and djurleite occurs in combination with twinning are particularly interesting because the two phases have different twin laws. One of the examples of the combination of epitaxy and twinning of anilite and djurleite is stereographically shown (Fig. 6).

NATURAL OCCURRENCES

Takeda *et al.* (1967) described a digenite-like phase together with djurleite in a specimen from Neudorf, Germany. The precession photographs of this digenite-like phase agree with those of anilite (Takeda, priv. commun. 1967). Clark and Sillitoe (priv. commun. 1969) confirmed the presence of anilite associated with djurleite and covellite in Estrella Mine, Atacama Province, Chili.

Because anilite changes to the digenite-type solid solution by grinding, and the latter cannot be distinguished from digenite by X-ray powder patterns, some of the reported associations of digenite and djurleite (Roseboom, 1966), examined by the powder method, could be that of anilite and djurleite.

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