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POLYMORPHISM IN DIGENITE

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ABSTRACT

Single-crystal investigations of synthetic as well as natural specimens have revealed the existence of three polymorphs of digenite. These are a high-temperature form, a low-temperature form, and a transitional metastable form, in close analogy with the bornite polymorphs described earlier. The high-temperature form is stable above 73° ± 3° C. and has cubic symmetry with $a = 5.570 \pm 0.005$ Å. The unit cell contains $Cu_{7.2-x}S_4$. The space group is *Fm3m*. The crystal structure of this polymorph was determined. The arrangement of the sulfur atoms is that of cubic closest packing, and 9/10 of the copper atoms occupy statistically 24 equivalent sites inside the sulfur tetrahedra. The coordinates are $x = 0.310$, $y = 0.300$, $z = 0.290$ for 7.2 Cu, and $x = y = z = 0$ for 4S.

The metastable form, which is obtained by cooling from 73° ± 3° C. or higher temperatures, has cubic symmetry with $a = 27.85 \pm 0.05$ Å and space group *Fd3m*. The special extinction rules observed among the x-ray reflections indicate that this cubic symmetry can be interpreted as due to twinning of fine domains with rhombohedral symmetry. This form is the same as that which was described as the low-temperature form of digenite ($a_{rh} = 16.16$ Å, $\alpha = 13°56'$) by Donnay *et al.* (1958). However, it was found to be transitional metastable in the present study. It changes gradually with time to a stable low-temperature form. This form also has cubic symmetry with $a = 27.85 \pm 0.05$ Å, without the special extinction rules. Its structure can be explained by twinning in the same way as that of the metastable form.

Synthetic material of exact Cu_9S_5 composition behaves slightly differently from natural digenite, suggesting that the composition of digenite should be formulated as $Cu_{9-x}S_5$. The thermal behavior of natural digenite is readily explained through its close analogy to that of synthetic $Cu_{9-x}S_5$.

INTRODUCTION

Digenite is a relatively common mineral occurring in small amounts in numerous important ore deposits where it commonly is associated with chalcocite and bornite. It forms over a wide range of geological conditions and has been reported to occur erratically distributed in some basic intrusives and occasionally disseminated in other basic rocks. Recently it has been reported as an exhalation product, and also occurs in some metamorphic rocks, in pegmatites, as a constituent of some high-temperature quartz veins, and even in many sediments. Digenite usually occurs in aggregates of anhedral grains but sometimes is found in well developed euhedral crystals. Previous studies of synthetic crystals indicated the existence of two polymorphs and an inversion temperature in the 47° to 80° C. range. The purpose of this investigation is to determine the temperature of inversion and to investigate the structures of the polymorphic forms.

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PREVIOUS INVESTIGATIONS

Donnay *et al.* (1958) reviewed the early literature on the structure of digenite. They also studied crystals of synthetic digenite by *x*-ray single-crystal methods and observed a reversible non-quenchable transition at about 65° C. in digenite of $Cu_{8.8}S_5$ composition. The low-temperature form of this material had a face-centered cubic lattice ($a = 27.71$ Å), which on the basis of extra-extinction rules was explained as the result of twinning of fundamental crystals having a rhombohedral cell ($a_{rh} = 16.16$ Å, $\alpha = 13°56'$). A tentative structure assuming the space group $R\bar{3}m$ was proposed on the basis of this rhombohedral cell.

Djurle (1958) also did *x*-ray studies on synthetic products and reported the inversion in Cu_9S_5 at 78° C.

The literature does not report any complete chemical analysis on digenite performed subsequent to its establishment as a mineral species. However, several analyses exist of "blue chalcocite," which Buerger (1941, 1942) showed to be identical with digenite. These analyses (Palache *et al.*, 1944) indicate that natural digenite takes some iron into solid solution. When iron is not present digenite apparently is of, or close to, Cu_9S_5 composition.

MATERIALS INVESTIGATED

Synthetic digenite. Digenite was synthesized by holding mixtures of copper and sulfur (of required composition) at fixed temperatures for various periods of time. The technique employed involves the use of rigid silica tubes. The products were chilled rapidly in cold water and identified at room temperature by optical and *x*-ray methods. Some of the digenite single crystals grown in this way were later investigated at elevated temperatures by Buerger's *x*-ray precession method.

Starting materials. Digenite of Cu_9S_5 composition was grown from mixtures of the elements without catalytic agents or additional components. The copper (99.999+per cent Cu) and sulfur (99.993+per cent S) used in these experiments were of the same materials used by Morimoto and Kullerud (1961).

Equipment. The experiments were performed as described by Morimoto and Kullerud (1961) for bornite synthesis. The free space in each silica tube was reduced as described by Kullerud and Yoder (1959). The vapor pressure over digenite is low. Accurate data are lacking, but Kushida (1952) reports a pressure of 22 mm Hg at 550° C. over a chalcocite-digenite mix-crystal without specifying exact composition. Sulfur cannot be distinguished as a phase over Cu_9S_5 crystals at 600° C. For these reasons negligible amounts of sulfur were lost to the vapor phase. The regrinding described for bornite synthesis (Morimoto and Kullerud,

1961) was not a necessary process for digenite synthesis, although when employed it shortens the required heating period for attainment of homogeneous digenite crystals. Starting with Cu and S a homogeneous digenite phase was obtained at 600° C. in less than 2 weeks. When the heating was interrupted by grinding after 24 hours, during which time all sulfur had reacted, only 6 days of additional heating were required to produce homogeneous digenite at 600° C.

Quench procedure. The silica tubes were plunged into water as quickly as possible at the termination of each experiment, reaching room temperature in a few seconds. The form of digenite that is stable at elevated temperatures cannot be retained even by the most rapid chilling, thus quenching of this form is not possible. However, the rate of chilling does influence the nature of the product. The effects of chilling are given later.

Description of the Cu_9S_5 *phase.* The morphology of digenite crystals, synthesized in a manner nearly identical to that employed in the present investigation, was described by Donnay *et al.* (1958). Our observations concur in all respects with those of Donnay *et al.*, and the morphology, therefore, will not be discussed here. The crystals used in our studies measured about 0.1×0.1×0.1 mm, but many were much larger. The maximum size was about 2×2×2 mm.

Natural digenite. We examined digenite crystals from two localities in the Leonard Mine, Butte, Montana. One of these specimens was obtained from the Smithsonian Institution (No. R 9925) and the other was collected by Kullerud.

X-Ray Studies

The Buerger precession method was used extensively, and the Weissenberg and oscillation methods were used frequently during the investigations of synthetic and natural digenites. The *x*-ray targets were Fe, Cu and Mo, with $K\alpha$ wave-lengths: Fe = 1.9373, Cu = 1.5418, and Mo = 0.7107 Å.

Because of the non-quenchable inversion occurring in the 47°–80° C. temperature range, it was necessary to study the crystals below, as well as above, the inversion temperature. The modified Buerger precession camera was used for this purpose (Morimoto and England, 1960; Morimoto and Kullerud, 1961). In this technique the mounted crystals are heated in air, and, although the highest temperature needed is only 80° C., caution is required to avoid oxidation of the crystals. The first *x*-ray photograph of each crystal was made at room temperature. After rapid heating the next photograph was made in 30 minutes to 1 hour at the desired temperature. The crystal was then cooled rapidly and a third exposure was made, again at room temperature. A final exposure was in each case made after storing the crystal in air at room temperature for 2 days. The first and last photographs of each crystal were identical, indicating that oxidation did not affect the crystal structure sufficiently to be detected by *x*-rays.

POLYMORPHISM

The metastable and the low-temperature forms. Crystals of composition $Cu_{9-x}S_5$ (where x varies from 0.05 to the value determined by the limit of solid solution of CuS or S in digenite at any given temperature) have a cubic cell when chilled from above the inversion temperature. The cell edge changes from 27.80 Å (5.56×5) for $Cu_{8.95}S_5$ to 27.70 Å (5.54×5) for $Cu_{9-x}S$ where $x=0.2$.

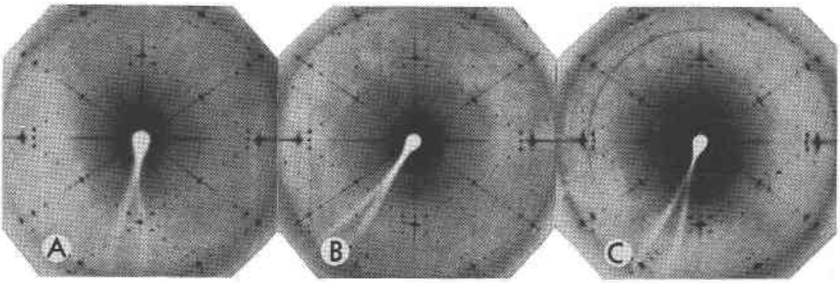

FIG. 1. Precession photographs of $(1\bar{1}0)_0^*$ of (a) synthetic digenite of $Cu_{8.95}S_5$ composition rapidly cooled from 600° C.; (b) natural digenite from Leonard Mine, Butte, Montana; and (c) synthetic digenite, Cu_9S_5, rapidly cooled from 300° C.

The precession photograph of $(1\bar{1}0)_0^*$ of a synthetic crystal of composition $Cu_{8.95}S_5$ and chilled from 600° C. is given in Fig. 1a. We refer to this form as the 5*a*-type because its cell length is five times that of the high-temperature form, which is described later and which we will refer to as the *a*-type.

Crystals of composition Cu_9S_5 and $Cu_{9+x}S_5$ also have a cubic cell when chilled from above the inversion temperature. When $x=0$ a cell dimension of $a=33.36$ Å (5.56×6) is obtained, and when $x=0.1$ a cell dimension of $a=33.42$ Å (5.57×6) is obtained. We refer to this form as the 6*a*-type. A precession photograph of $(1\bar{1}0)_0^*$ of the 6*a*-type is shown in Fig. 1c. This material, which has the composition $Cu_{9+x}S$, where $x=0.05$, was chilled from 300° C. The precession photographs of both the 5*a*- and 6*a*-types show superstructure reflections located at equal intervals between the main reflections due to the fundamental sub-cell.

Donnay *et al.* (1958) observed the 5*a*-type structure in the material with $a=5.54$ Å and composition $Cu_{8.8}S_5$.

Buerger (1942) did not observe certain reflections ($119_c = 223_{rh}$, and $991_c = 665_{rh}$) which are more intense in the $5a$-type than other reflections that he did observe such as 222 (or 10,10,10, referred to the large cube). This indicates that Buerger (1942) in reality observed the $6a$-type structure in which the 119_c and 991_c reflections are extinct. Further evidence that Buerger (1942) observed the $6a$-type is the cell dimension of $a = 5.565$ Å (calculated from d values given in Table 1 of Buerger, 1942), which indicates about $Cu_{9.05}S_5$ composition.

Donnay *et al.* (1958) pointed out two characteristic properties of the chilled products: (1) the superstructure with a fundamental sub-cell ($a = 5.54$–5.56 Å) and (2) the special extinction rules for the superstructure reflections. The diamond-shaped areas with complete lack of reflections in Fig. 1a and Fig. 1c demonstrate that only the reflections $10m \pm L$, $10n \pm L$, L occur in the $5a$-type and that only the reflections $12m \pm L$, $12n \pm L$, L occur in the $6a$-type structure.[1]

TABLE 1. X-RAY DETERMINATION OF THE TEMPERATURE OF THE DIGENITE INVERSION

a. Cu_9S_5 synthesized at 600° C.		b. $Cu_{9.01}S_5$ synthesized at 300° C.	
T, ° C.	Form	T, ° C.	Form
25	modified $6a$	25	modified $6a$
82	high (a)	85	high (a)
74	high (a)	81	high (a)
72	$6a$	80	high (a)
25	modified $6a$	72	$6a$
		67	$6a$
		25	modified $6a$

However, the special extinction rules only apply for a limited time after the crystals have been chilled. Re-examination of crystals after they have been stored in air for 2 days reveals the appearance of weak intensity reflections which void the special extinction rules both for the $5a$- and $6a$-type structures. Of these new reflections the most remarkable are the 577_c and $5.5.10_c$ in the $5a$-type and the $6.6.11_c$ and $6.6.13_c$ in the $6a$-type. The intensities of the new reflections increase noticeably over a period of several days subsequent to the chilling. The superstructures containing these additional reflections are referred to below as the modified $5a$- and the modified $6a$-types.

The changes in the modified $5a$-type were completed after 5 days. Further changes were not observed even after the crystal had been kept for many months in air and at room temperature.

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[1] m and n represent any integer including zero.

The pattern of the modified 5*a*-type is shown in Fig. 1b, which is a precession photograph $(1\bar{1}0)_0^*$ of digenite from Leonard Mine, Butte, Montana. The modified 5*a*-type, therefore, is stable and the 5*a*-type is metastable at room temperature.

Crystals with the 6*a*-type structure when kept in air at room temperature first change in a matter of hours to the modified 6*a*-type structure, which persists for 3 weeks to several months depending on the value of x in $Cu_{9+x}S_5$. After this period of time structural changes are observed in the x-ray patterns. Crystals with $0<x<0.1$ gradually develop the structural characteristics of the modified 5*a*-type, and their patterns after several months show all the details of the modified 5*a*-type with no additional reflections. Under the outlined conditions this type remains unchanged even after 2 years.

Crystals of $Cu_{9+x}S_5$ composition, where $x \geq 0.2$, also first develop the modified 6*a*-type structure, but on further storage behave differently from the crystals with $0<x<0.1$. A complex pattern, apparently indicating the presence of two phases, gradually develops. The patterns show the modified 5*a*-type reflections and additional remarkably different reflections. Morimoto (1962) has recently shown that these additional reflections are due to a compound of approximately $Cu_{1.96}S$ composition. The stability of this compound is evidenced by its occurrence in nature as the mineral djurleite (Morimoto, 1962).

Although digenite and bornite form a complete solid-solution series at high temperatures (Kullerud, 1960), the x-ray reflections of low-temperature digenite are quite different from those of low-temperature bornite. All the reflections of the latter are explained based on space group $P\bar{4}2_1c$ or on twinning (rather macroscopic) of this space group. Digenite, however, does not show any evidence of this type of twinning in the specimens examined, and all the reflections are described by space group $Fd3m$. This difference suggests that the transition mechanisms from the metastable forms to the low-temperature forms are slightly different for digenite and bornite.

The high-temperature form. In order to investigate the high-temperature form natural digenite (modified 5*a*-type) and synthetic digenite of the 6*a*-type were examined. The modified Buerger precession camera (Morimoto and Kullerud, 1961) was used for this purpose.

The precession photographs of Fig. 2 taken in the $(1\bar{1}0)_0^*$ direction are of digenite from Leonard Mine, Butte, Montana: (*a*) at room temperature before heating, (*b*) while heated at 80° ± 3° C., and (*c*) at room temperature within a few hours after heating. All exposures were of 30 minute duration and were made with Cu radiation (45 KV, 20 MA) without filter. The superstructure reflections of Fig. 2a, including strong reflec-

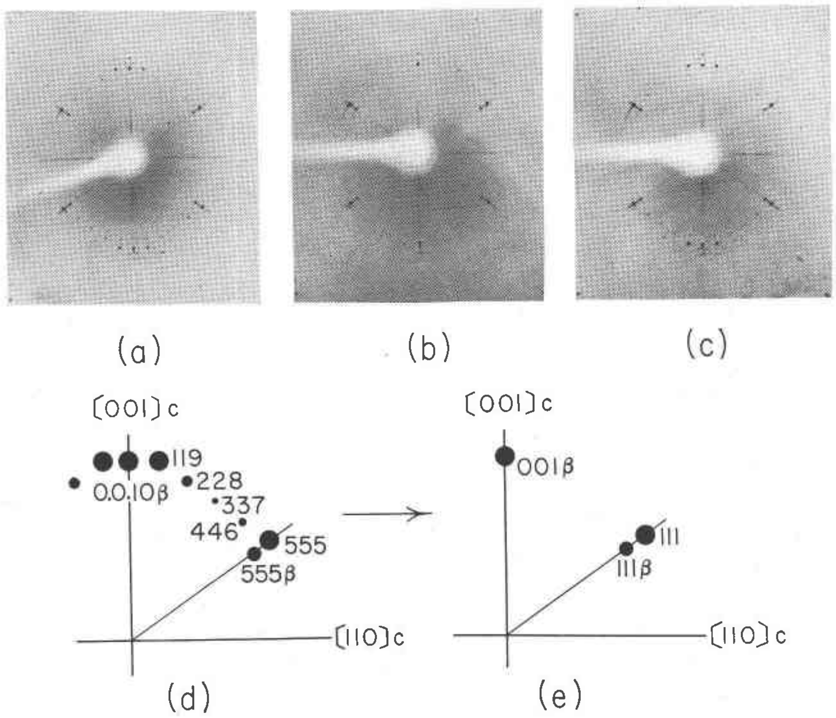

FIG. 2. Precession photographs of $(1\bar{1}0)_0^*$ of natural digenite, Leonard Mine, Butte, Montana, taken (a) before heating, (b) at 80° ± 3° C., and (c) shortly after heating (30 minutes exposure, CuKα, 45 KV, 20 MA, without filter). The precession diagrams of (a) and (b) are given in (d) and (e), respectively, with reflection indices.

tions such as 119_c, disappear on heating to 80° C., as seen in Fig. 2b. Schematic diagrams and indices demonstrating the change due to heating are given in Fig. 2d and e.

The cell constants obtained from the precession photographs are: $a = 5.552 \times 5$ Å for the modified $5a$-type (Fig. 2a), $a = 5.567$ Å for the high-temperature form (Fig. 2b), and $a = 5.557 \times 5$ Å for the $5a$-type (Fig. 2c). The high-temperature form of digenite is isostructural with that of bornite (Morimoto and Kullerud, 1961).

Temperature of inversion. Synthetic materials of, or close to, Cu_9S_5 composition were also studied by the modified Buerger precession method in order to determine the temperature of the inversion. The results of these experiments, given in Table 1, indicate that the inversion takes place at 73° ± 3° C.

The Cu_9S_5 and $Cu_{9.01}S_5$ materials were chilled from the temperatures of synthesis and x-rayed a few hours later. Both showed the pattern of the modified 6a-type structure. Then the materials were heated at the temperatures indicated in Table 1a and b. Each exposure lasted from 30 minutes to 1 hour, and the desired changes in temperature after each exposure were accomplished in less than 10 minutes. Each sample was immediately cooled to room temperature (25° C.) at the termination of the heating experiments. Final exposures 1 to 2 hours after cooling gave the modified 6a-type structure for Cu_9S_5 as well as $Cu_{9.01}S_5$.

CRYSTAL STRUCTURES

The high-temperature form. In order to determine the structure, precession photographs $(1\bar{1}0)_0^*$ of natural digenite, from Leonard Mine, Butte, Montana, were taken at 80°±3° C. with Mo radiation ($MoK\alpha = 0.7107$ Å) and exposures varying from 30 minutes to 3 hours. The size of the specimen was about 0.05×0.05×0.05 mm. All intensities of the reflections (*hhl*) were measured by the photometer. The relative intensities were determined considering the differences in the exposures and were corrected for Lorentz and polarization factors. Corrections were not applied for absorption and extinction. The relative F values were transposed to the absolute scale in a later stage of analysis to give $\sum|F_{obs.}| = \sum|F_{calc.}|$, excluding $F_{obs.}=0$. The space group of the high-temperature digenite is $Fm3m$. The unit cell with $a=5.57$ Å contains $Cu_{7.2}S_4$. The antifluorite model, first proposed by Barth (1926), was discarded by Ralhfs (1936) because the model could not explain the experimental data. Ralhfs, on the basis of sulfur distribution of a face-centered cubic lattice with $a=5.56$ Å, assumed that Cu atoms were located in one of three kinds of positions—centers of triangles, of tetrahedra, or of octahedra, with sulfur atoms at the corners. He calculated all the various intensities arising from changing the distribution weights of the Cu atoms in these three kinds of positions. However, no combination led to agreement between calculated and observed intensities, and he concluded that no cubic structure was possible for high-temperature digenite.

We also assumed that all sulfur atoms occupy nodes of a face-centered cubic lattice, and determined the positions of the Cu atoms. The calculated structure factors on the basis of the antifluorite structure in which 9/10 Cu is at the center of each sulfur tetrahedron disagree with the observed values as shown in Table 2. The Cu atoms were next assumed to be statistically distributed in the sulfur tetrahedra. The best fit between observed and calculated structure factors is obtained when 9/10 of a Cu atom is statistically distributed over 24 equivalent sites in each of the sulfur tetrahedra. Thus 7.2 Cu atoms are statistically distributed over 24×8=192 sites in the unit cell, and the sulfur atoms build a face-

TABLE 2. THE ATOMIC COORDINATES OF HIGH-TEMPERATURE DIGENITE

Atom	No. of positions (notation)	No. of atoms	x	y	z
S	4 (a)	4	0	0	0
Cu	192 (c)	7.2	0.310	0.300	0.290

centered close-packing. This structure is schematically shown in Fig. 3. The atomic coordinates are given in Table 3. The calculated values of structure factors are given in Table 2. Temperature factors used are $B = 2.0$ for the sulfur atoms and $B = 4.0$ for the copper atoms. The R factor for fifteen reflections is 12.6 per cent including reflections not observed.

It is of interest that the Cu atoms are statistically distributed over 192

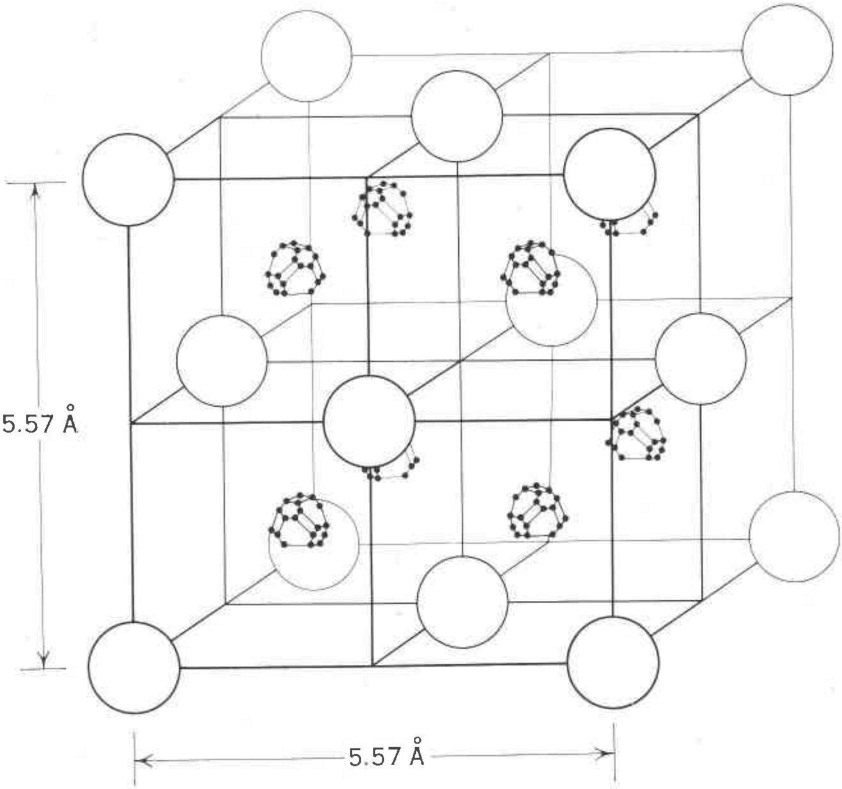

FIG. 3. The structure of high-temperature digenite. Large white circles, sulfur atoms; black circles, statistically distributed copper atoms.

equivalent sites inside the sulfur tetrahedra even at a temperature as low as 80° C. This is exactly the same situation as was observed in bornite at 240° C. (Morimoto, in preparation). Although this structure is slightly different from the "liquid-like" structure found in α-AgI (Strock, 1934, 1935), it is certain that the Cu atoms are in a "mobile" state. The identity with bornite explains the complete solid solution between the two minerals above the inversion temperature (Kullerud, 1960).

The metastable and the low-temperature forms. The crystal structures of the metastable and the low-temperature forms are closely related, but the metastable form is somewhat less complex than the modified 5*a*-type.

TABLE 3. COMPARISON BETWEEN OBSERVED AND CALCULATED STRUCTURE FACTORS IN THE HIGH-TEMPERATURE DIGENITE

hkl	$F_{\text{obs.}}$	Antifluorite structure	Final structure
002	74	−112.8	−74.4
004	54	109.4	57.4
006	—	−36.4	6.2
111	49	45.5	43.7
113	37	30.0	32.8
115	10	17.6	15.8
220	109	152.6	111.2
222	26	−70.8	−23.8
224	37	87.2	35.3
331	10	24.0	18.8
333	35	20.8	32.3
335	—	12.0	4.8
440	25	69.0	22.1
442	—	−31.6	9.0
444	10	44.5	10.6

Donnay *et al.* (1958), who observed the metastable form of synthetic digenite, on the basis of a twinning hypothesis derived the fundamental rhombohedral sub-cell with space group $R\bar{3}m$ and explained the special extinction rules for the superstructure reflections.

This rhombohedral cell has $a_{\text{rh}} = 16.16$ Å, $\alpha = 13° \, 56'$, and contains one Cu_9S_5. The rhombohedral crystals are in twin relation with $\overline{337}_{\text{rh}}$ as the twin axis producing cubic symmetry collectively.

Based on studies of the crystal structure of bornite (Morimoto, in preparation), the superstructure of the metastable (5*a*) form of digenite can be explained as in Fig. 4b on the basis of the rhombohedral cell. This superstructure is derived from the high-temperature form in which sulfur atoms occupy the nodes of the cubic face-centered lattice and each tetra-

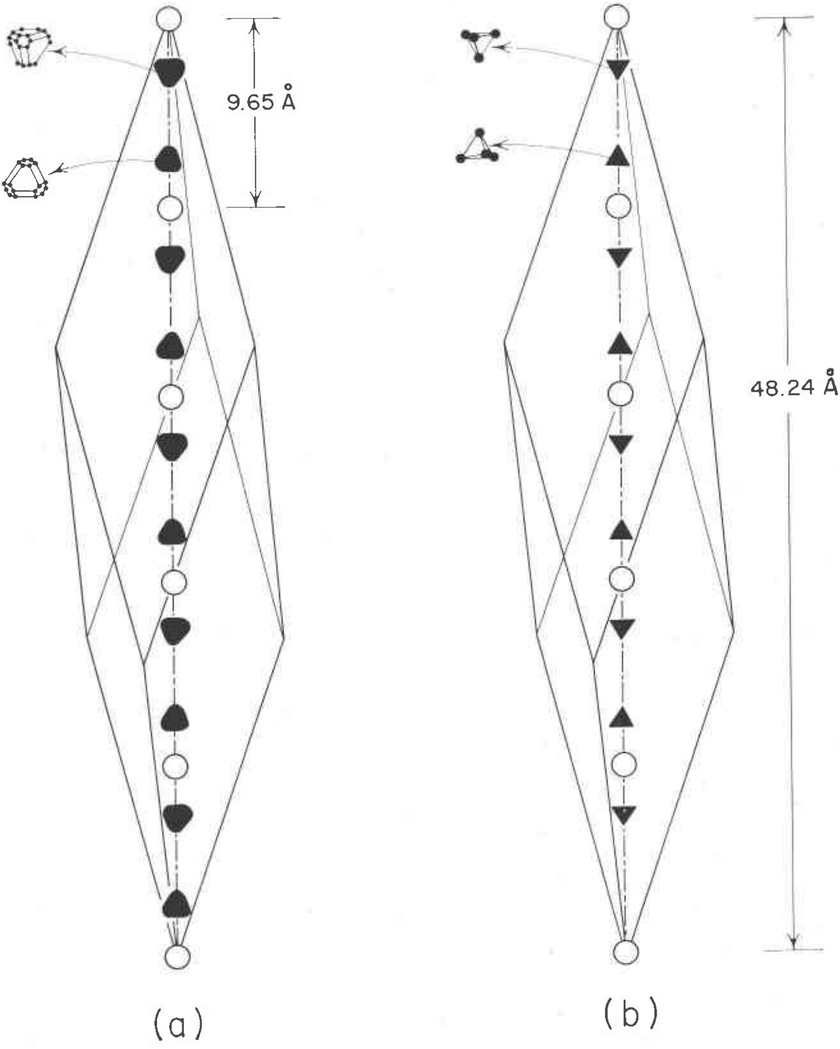

FIG. 4. The crystal structure of (a) high-temperature digenite and (b) metastable digenite. The body diagonal [111] is drawn through five unit cells of the high-temperature form to illustrate similarities with the rhombohedral cell of the metastable form.

hedron contains 9/10 Cu atom which is statistically distributed at 24 equivalent positions. The structure of the high-temperature form can be interpreted as stacking of S and Cu layers which are all parallel to (111) (Fig. 4a). The order of the layers is represented as Cu S Cu Cu S Cu Cu

S Cu —. If we take an S layer sandwiched by two Cu layers, CuSCu, as unit, the structure may be described as stacking of sandwiches. Now, if we were to take away one Cu layer from every fifth sandwich and redistribute equally these Cu atoms among the remaining nine Cu layers, we would obtain the structure of the metastable form. In this structure each sulfur tetrahedron contains 1.0 Cu atom. Instead of statistical distribution of the Cu atoms over 24 equivalent positions in the sulfur tetrahedra as in the high-temperature form, the Cu atoms are in the metastable form statistically distributed in only four equivalent positions, in the same way as in the metastable bornite.

Thus, in the transition from the high-temperature to the metastable form, all sulfur atoms and $\frac{8}{9}$ of all Cu atoms stay approximately in their original positions and only $\frac{1}{9}$ of the Cu atoms migrate or diffuse in the structure to produce vacant positions. These relations are given schematically in Fig. 4. This transition mechanism implies a very small ΔH and explains why we were not able to detect the inversion by DTA experiments.

The low-temperature form of digenite has additional reflections which modify the 5*a*-type of the metastable form. This modified 5*a*-type structure has the same cell size and space group *Fd3m* as the original 5*a*-type structure. Although the special extinction rules for the reflections do not exist in the low-temperature form, the intensities of the additional reflections are generally very weak, except $(557)_c$ and $(5.5.10)_c$. For this reason it is assumed that the low-temperature form represents an ordering of the metastable form. The ordering may be ascribed to the preferential occupation of Cu atoms among the four possible positions in the sulfur tetrahedra and some adjustments among the sulfur atoms surrounding the Cu atoms.

Natural digenite. One of the two studied digenite specimens from Leonard Mine, Butte, Montana, has well developed crystal faces and contains some exsolved bornite. The crystals of the second specimen (obtained from the Smithsonian Institution, No. R 9925) are not euhedral but show good cleavage parallel to (111). This specimen also contains some bornite and djurleite (Morimoto, 1962). Digenite crystals from both specimens were examined with the precession camera and were found to possess the modified 5*a*-type structure given in Fig. 1b.

The fact that compounds with exact Cu_9S_5 or $Cu_{9+x}S_5$ composition show first 6*a*-type structure and then finally change to the modified 5*a*-type and djurleite indicates that digenite has $Cu_{9-x}S_5$ composition or even $(Cu, Fe)_{9-x}S_5$ where some small amounts of iron may substitute for cop-

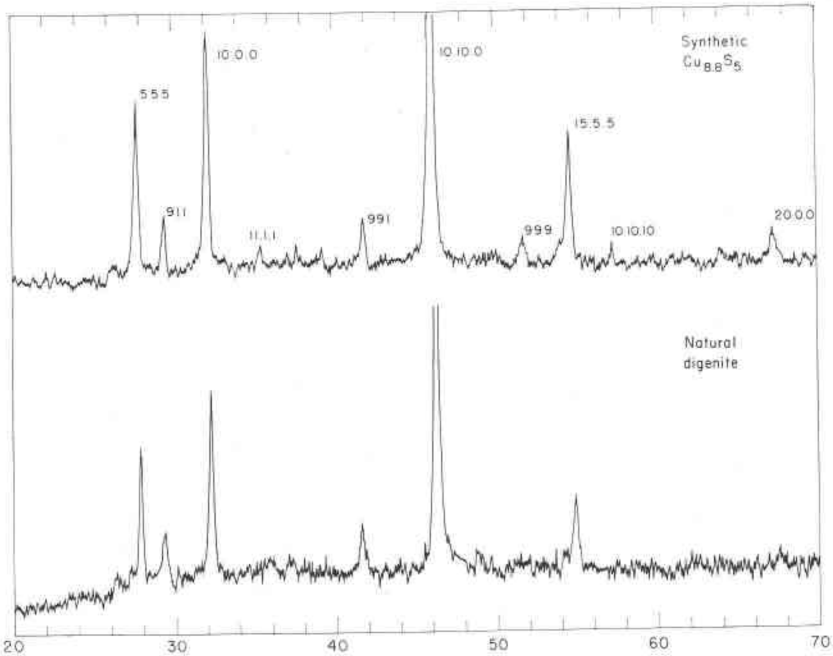

FIG. 5. The powder patterns of synthetic $Cu_{8.8}S_5$ with the modified 5*a*-type structure and digenite, Leonard Mine, Butte, Montana.

per. The powder patterns of natural digenite and the synthetic 5*a*-type are given in Fig. 5.

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