CRYSTAL AND TWIN STRUCTURE OF DIGENITE,[1] Cu_9S_5

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ABSTRACT

Digenite undergoes a rapidly reversible and non-quenchable transformation between 60 and 65° C. Digenite was synthesized in octahedra modified by small cube faces. Single-crystal methods yield a cubic cell whose edge a is equal to five times the literature value: $a = 27.71$ Å $\pm 0.3\%$. With 100 Cu_9S_5 per cell, the calculated specific gravity is 5.715, against 5.6 observed. Only HKL reflections observed are of the type $10m \pm L$, $10n \pm L$, L, with m and n integers. The numerous structural absences are explained by twinning; the octahedron consists of four rhombohedral crystals, oriented with their hexagonal c axes along the body diagonals and their hexagonal a axes along the face diagonals of the simulated cubic cell. The twin axis is $[\overline{3}3\overline{7}]$ in rhombohedral notation; twin index 5; twin obliquity 0. The rhombohedral cell ($a = 16.16$ Å, $\alpha = 13° 56'$) contains one Cu_9S_5. The diffraction aspect is R^{**}. The pronounced pseudo-cube, $a' = a/5 = 5.54$ Å, is explained as follows. Only those reflections whose cubic indices HKL are multiples of 5 receive contributions from all four crystals of the twin; they are the only reflections, moreover, to which sulfur atoms contribute. Space group $R\overline{3}m$ leads to a tentative structure in which all atoms lie on the 3-fold axis of the rhombohedral cell, in positions xxx. For the five sulfur atoms, the values of x are: 0, $\pm 1/5$, $\pm 2/5$; for the nine copper atoms: 1/2, ± 0.060, ± 0.133, ± 0.250, ± 0.350.

HISTORICAL

Rahlfs (1936) synthesized Cu_9S_5 and took powder patterns at 170° C. He found a face-centered cubic lattice with cell edge equal to 5.575 ± 0.016 Å (Å from kX) and a cell content of $Cu_{7.2}S_4$. He also noted that up to 600° C. no transition to a polymorphic form occurs. In a very thorough attempt at elucidating the crystal structure, Rahlfs placed the sulfur atoms at the nodes of the face-centered lattice. This close-packed arrangement is found in a host of sulfide structures, such as ZnS (sphalerite), CaS, PuS, US, which have a cubic cell of about the same size. He tried placing the copper atoms in all the possible holes left by the close-packed sulfur atoms in a way that would keep the symmetry cubic, namely at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ and $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ in tetrahedral coordination, $\frac{1}{3}\frac{1}{3}\frac{1}{3}$ and $\frac{2}{3}\frac{2}{3}\frac{2}{3}$ in trigonal coordination and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ in octahedral coordination. No combination of these sites led to any agreement between calculated and observed intensities of the powder pattern, so that Rahlfs was driven to the conclusion that no cubic structure was possible. No further word on the crystal structure of Cu_9S_5 as such has appeared in the literature, but Ross (1954) proposed a theory according to which at least some of the copper atoms in the structure are mobile. Diffuse intensity regions in

reciprocal space would be predicted on the basis of such a hypothesis. Molé (1954) synthesized crystals of digenite by passing H_2S gas over single crystals of CuCl. He reports obtaining digenite at 800° C. with a pseudo-cubic lattice and cell edge equal to 22.4 Å. He gives no details as to the true symmetry of his diffraction patterns. (Note that $22.4 = 4 \times 5.6$.)

Buerger (1942) cleared up the confusion that still existed in the mineralogical world concerning the so-called "high-temperature, blue, or isometric chalcocite" by showing that its powder pattern is identical with that of Cu_9S_5. For this, the only known intermediate compound in the CuS—Cu_2S phase diagram, he proposed to revive the mineral name digenite,[1] a name originally given to a hypothetical compound Cu_5S_4. In his doctoral dissertation (1940, unpublished) Buerger states: "It is likely that at a temperature of 47° C. or lower the copper atoms become ordered and give rise to another digenite phase."

SYNTHESIS

Digenite was synthesized during a current study of the copper-sulfur system. Chalcocite Cu_2S, digenite Cu_9S_5, and covellite CuS are the three known compounds in this system. All experiments were carried out in evacuated and sealed silica glass tubes. The copper used in all experiments was standard sample 45C of the National Bureau of Standards (analyzed 99.99% Cu). Sulfur purified to analyze 99.993% S and 0.007% C was kindly supplied by Dr. W. N. Tuller, Superintendent of Laboratory, Freeport Sulphur Co., Port Sulphur, La.

In experiments with copper and sulfur in the atomic ratio of 1:1 and where the charge occupied $\frac{1}{2}$ to $\frac{1}{3}$ of the tube volume, covellite was found to form as the only solid phase up to about 250° C. Above this temperature the dissociation pressure of covellite leads to the formation of a sulfur-rich vapor phase. The copper-to-sulfur atomic ratio in the solid becomes larger than 1:1 and a mixture of digenite and covellite coexists with the vapor. At increasing temperatures digenite, covellite, and vapor, under these specified volume conditions, coexist up to about 400° C. At this temperature all covellite has decomposed, and digenite and vapor are the only phases present. Since covellite is the most sulfur-rich compound in the Cu—S system, the maximum temperature at which it can exist in rigid silica tubes was determined by addition of sulfur to the charge. $CuS + L + V$ were found to coexist up to $507 \pm 3°$ C. Above this temperature $Cu_9S_5 + L + V$ are stable together. At this invariant point the four phases $Cu_9S_5 + CuS + L + V$ are all stable. Starting with copper and sulfur in the atomic ratio of 9:5, digenite still grows at 775° C. The

[1] Ramdohr later proposed the name neodigenite for Cu_9S_5.

invariant point where the four phases $Cu_2S + Cu_9S_5 + L + V$ are all stable has as yet not been determined.

With copper and sulfur in the atomic ratio 9:5, the lowest temperature at which digenite was synthesized is 25° C. Reaction between copper and sulfur was noticeable after only 24 hours, but even after 5 months the tubes still contained small amounts of copper and sulfur which had not reacted. At 90° C. all copper had reacted with sulfur to form digenite in about 8 weeks, at 200° C. in about 2 weeks, and at 400° C. in less than 2 days.

Runs containing copper and sulfur in the atomic ratio of 8.5:5[1] and in which the charge occupied about $\frac{1}{3}$ of the tube volume produced digenite and covellite at 300 and 350° C., and digenite and sulfur at 400, 500 and 650° C. This shows that the atomic percentage of sulfur, which is 35.7 in Cu_9S_5, cannot exceed 37.0 in a digenite solid solution. Runs at 500° C. containing copper and sulfur in the atomic ratio of 9.2:5 produced chalcocite and digenite, showing that if digenite can take up copper in solid solution, the maximum amount, at least at this temperature, is less than 0.5 atomic per cent. The cell dimensions of digenite formed at various temperatures and from mixtures where the copper-to-sulfur ratio varied from 6:5 to 9.5:5 were determined by x-ray diffraction methods. The cell size, however, within the limits of our experimental accuracy (0.3% on lengths) remains constant. "Single crystals" of digenite were produced in more than 30 runs. The crystals used for single-crystal investigations were synthesized at temperatures between 150° C. and 600° C. The digenite "single" crystals always occurred as octahedra, occasionally extremely malformed and frequently modified by small cube faces. Two opposite octahedral faces sometimes predominate over all other faces to such an extent that the crystal looks like a flat hexagonal plate. The crystals vary in size from 10 μ (crystals formed in 4 months at 150° C.) to 4 mm. (crystals formed in the same length of time at 600° C.).

It was observed that, at temperatures above the covellite stability field, digenite crystals grow to a larger size when the copper-to-sulfur ratio is smaller than 9:5, than when the ratio is equal to or larger than 9:5 (but smaller than 2:1).

Accompanying this variation in rate of growth is a striking change in crystal morphology (Figs. 1a and 1b). Crystals which grow from mixtures where the copper-to-sulfur ratio is smaller than 9:5 have perfectly rounded edges, while those which grow from mixtures where the copper-to-sulfur ratio is larger than 9:5 (but smaller than 2:1) have stepped faces due to oscillation of cube and octahedron. Crystals grown from

[1] Cu and S in atomic ratio 8.5:5 corresponds to 37.0 atomic % S.

mixtures where the copper-to-sulfur ratio is exactly 9:5 show neither of these features.

Digenite was studied on the temperature controlled Norelco diffrac-
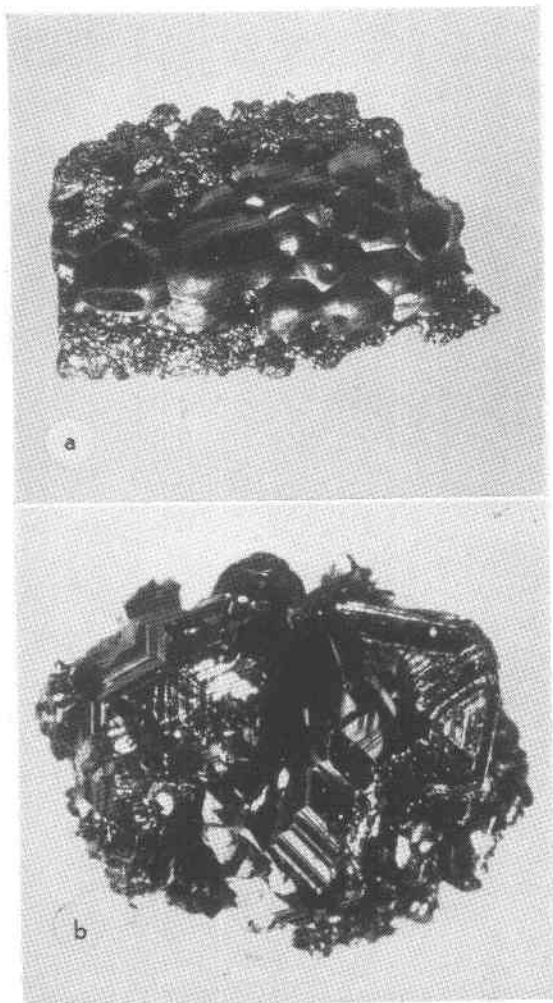
FIG. 1. Crystals of digenite grown at 500° C. for 130 days. (*a*) Bulk composition $Cu_{8.6}S_5$. Magnification 12×. (*b*) Bulk composition $Cu_{9.2}S_5$. Magnification 25×.

tometer designed by Mauer and Bolz (1955) at the National Bureau of Standards. We found it to undergo a rapidly reversible and non-quench-able inversion between 60 and 65° C. The flat powder specimen was repeatedly heated and cooled through the inversion temperature, in an

atmosphere of helium to prevent oxidation. The weak reflections of the low-temperature phase, which cannot be indexed on the basis of the 5.57 Å cubic face-centered cell, disappeared and reappeared each time.

Dr. A. D. Franklin, Ferroelectricity Group, National Bureau of Standards, kindly measured the electrical resistance of digenite while varying the temperature. His preliminary results are not sufficient defi-
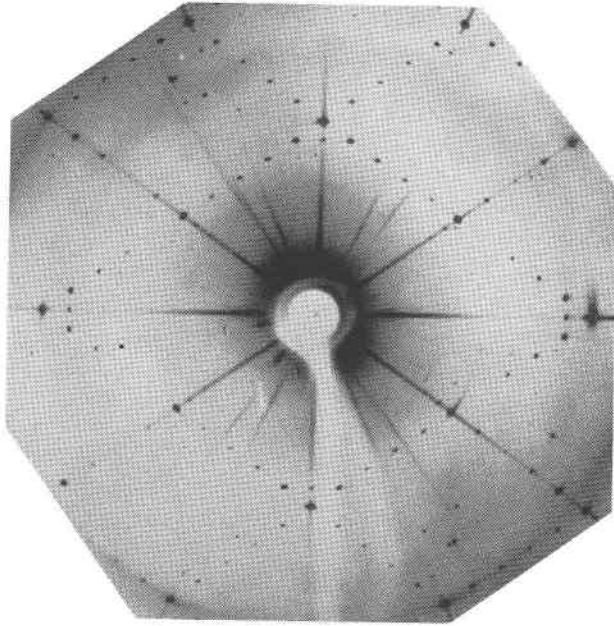
Fig. 2. Precession film $(1\bar{1}0)_c{}^*$ containing reflections HHL; only reflections of the form $10m \pm L \cdot 10m \pm L \cdot L$ are observed. Cu Kα, 15 hours.

nitely to confirm the existence of the transition, although they indicate that on cooling a large peak repeatedly appears in the neighborhood of 60° C. in the curve of resistance vs. temperature. He reports that much more precise measurements would be necessary to ascertain the behavior.

X-Ray Data

We obtained single-crystal patterns with CuKα ($\lambda = 1.5418$ Å) and MoKα ($\lambda = 0.7107$ Å) radiations, using the precession as well as rotation and Weissenberg cameras. A precession photograph of $(1\bar{1}0)_c{}^*$ (Fig. 2) shows that at room temperature $a_c' = 5.54 \pm 0.02$ Å (subscript c refers to cubic interpretation) is only a pseudo-repeat, albeit a pronounced one. The true repeat appears to be $a_c = 5a_c' = 27.71$ Å. The cell volume is thus multiplied by 125 and the cell content is increased from 0.8 Cu$_5$S$_5$

to 100 Cu_9S_5. The striking feature of the net $(1\bar{1}0)_c{}^*$ of the reciprocal lattice is the extremely large number of structural absences: only reflections of the form HHL, with $H = 10m \pm L$ (m integer), are present. A rotation pattern about the a_c axis (Fig. 3) illustrates well the systematic nature of structural absences throughout reciprocal space. Complete indexing of Weissenberg patterns shows that, without exception, all the
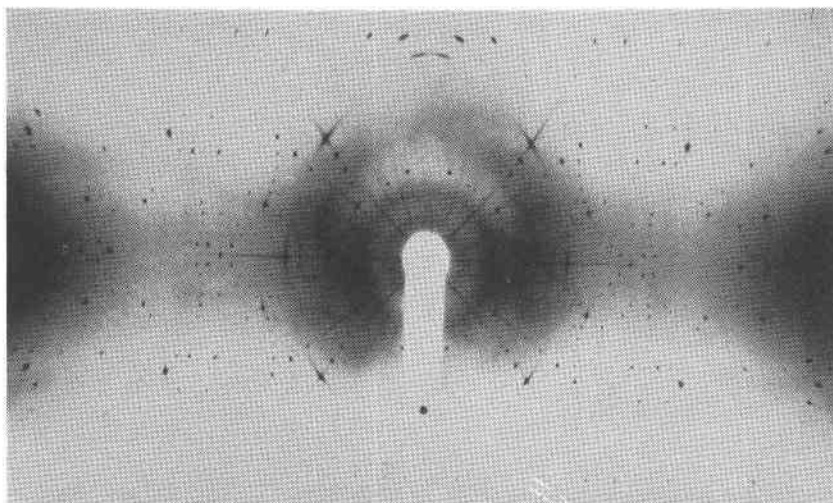
FIG. 3. Rotation pattern about a_c. Note large number of absent reflections on all layer lines. Cu Kα, 19 hours.

reflections are of the type $10m \pm L$, $10n \pm L$, L (m, n integers). As the indices of these reflections are all odd or all even, the diffraction aspect is F^{***}.

We faced the problem of placing 900 copper atoms and 500 sulfur atoms in the large face-centered cube in such a way that the observed structural absences would result. This proved to be impossible in any of the permitted space groups.

TWINNING HYPOTHESIS

In a study of sodium peroxide III, Carter and Templeton (1953) had encountered an unusually large number of structural extinctions of x-ray reflections, and a twinning hypothesis had provided a satisfactory interpretation. Dr. David Templeton, to whom we mentioned our problem, immediately suggested that we look into the possibility of twinning. What follows will show how indebted we are to him for this advice.

If our digenite "crystals" are twins, the observed octahedral habit of

the twin can be explained by associating the individual crystals with the body diagonals of the cube. Each crystal must therefore be hexagonal *s.v.;* its lattice can be either hexagonal or rhombohedral. According to the Law of Bravais the axial ratio c/a must be large enough to account for the predominance of the base, which is to form the octahedral face of the twin—$c/a > 0.87$ if the lattice is hexagonal; $c/a > 2.3$ if it is rhombohedral (see nomograms in Mallard, 1879). As to symmetry, the point group of
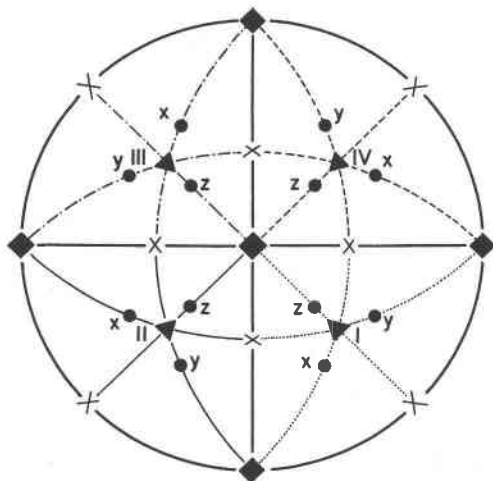
FIG. 4. Stereographic projection of twin on $(001)_c$. The 4-fold twin axis $[001]_c$ brings individuals I, II, III, and IV to coincidence.

the crystal must be a subgroup of the point group of the twin, so that the symmetry operations of the individual crystals, combined with the twin operations, will generate the point group of the twin. If, as in the present case, the observed twin symmetry is $4/m \ \overline{3} \ 2/m$, the crystal symmetry must be at least $\overline{3} \ 2/m$ if the twin operation is a 90° rotation about any of the three 4-fold symmetry axes of the twin or a reflection in any of the mirrors perpendicular to these 4-axes. (Rigorously speaking, provided the crystal lattice were hexagonal, the crystal symmetry could even be a supergroup of $\overline{3} \ 2/m$, but in this case the additional symmetry operations of the crystal would be lost in twinning and would not appear among the symmetry operations of the twin symmetry $4/m \ \overline{3} \ 2/m$.) A stereographic projection on $(001)_c$ (Fig. 4) shows how the symmetry elements of the twin can be subdivided into twin elements, on the one hand, and symmetry elements of four individual crystals, on the other. Let us agree to use $[001]_c$ as 4-fold twin axis, so that crystal I will be brought to coincidence with crystals II, III, IV by clockwise rotations of 90°, 180°, 270°, respectively.

Because the twin lattice extends without deviation throughout the twin edifice, the *twin obliquity* is zero, and we are dealing with twinning by reticular merohedry (Friedel, 1926) on the assumption of a rhombohedral crystal lattice. The twin axis is [$\overline{3}37$], referred to the rhombohedral axes of each crystal. The *twin index* is 5. This twin arrangement leads to

TABLE 1. TRANSFORMATION OF INDICES

Matrices *s: rhombohedral from cubic*

Crystal I			Crystal II			Crystal III			Crystal IV		
.4	.3	.3	.3	$.\overline{4}$	.3	$.\overline{4}$	$.\overline{3}$	.3	$.\overline{3}$	.4	.3
.3	.4	.3	.4	$.\overline{3}$	.3	$.\overline{3}$	$.\overline{4}$	.3	$.\overline{4}$	.3	.3
.3	.3	.4	.3	$.\overline{3}$	.4	$.\overline{3}$	$.\overline{3}$	.4	$.\overline{3}$	.3	.4

Matrices *t: cubic from rhombohedral*

Crystal I			Crystal II			Crystal III			Crystal IV		
7	$\overline{3}$	$\overline{3}$	$\overline{3}$	7	$\overline{3}$	7	3	3	3	7	3
$\overline{3}$	7	$\overline{3}$	7	3	3	3	7	3	7	$\overline{3}$	$\overline{3}$
$\overline{3}$	$\overline{3}$	7	$\overline{3}$	$\overline{3}$	7	$\overline{3}$	$\overline{3}$	7	$\overline{3}$	$\overline{3}$	7

the following *s* matrices (Int. Tab., Vol. I, 1951, p. 15), that must be used to obtain rhombohedral indices *hkl* from cubic ones *HKL*, one matrix for each of the four individuals. The inverse *t* matrices permit us to obtain cubic indices *HKL* from rhombohedral ones, *hkl* (Table 1).

The explanation of the cubic absences follows at once. Let us designate by $H_jK_jL_j$ the cubic indices of a given *hkl* reflection coming from the *j*th crystal, *j* = I, II, III, IV. The *t* matrices (Table 1) give, setting $s = 3(h+k+l)$:

$$H_I = 10h - s, \qquad K_I = 10k - s, \qquad L_I = 10l - s,$$
$$H_{II} = 10k - s, \qquad K_{II} = -(10h - s), \qquad L_{II} = 10l - s,$$
$$H_{III} = -(10h - s), \qquad K_{III} = -(10k - s), \qquad L_{III} = 10l - s,$$
$$H_{IV} = -(10k - s), \qquad K_{IV} = 10h - s, \qquad L_{IV} = 10l - s.$$

We drop the subscript from the *L* index and substitute $(10l - L)$ for *s* in the expressions of H_j and K_j. We thus obtain, setting $m = h - l$ and $n = k - l$:

$$H_I = 10m + L, \qquad K_I = 10n + L, \qquad L_I = L,$$
$$H_{II} = 10n + L, \qquad K_{II} = -(10m + L), \qquad L_{II} = L,$$
$$H_{III} = -(10m + L), \qquad K_{III} = -(10n + L) \qquad L_{III} = L,$$
$$H_{IV} = -(10n + L), \qquad K_{IV} = 10m + L, \qquad L_{IV} = L.$$

These relations show that every H or K cubic index will be "a multiple of $10 \pm$ the index L," as observed.

Note that the general set of reflections in space group $R\bar{3}m$ consists of twelve symbols, which correspond to the twelve faces of the hexagonal scalenohedron. In rhombohedral axes, they are the six permutations of

Fig. 5. Precession pattern $(1\bar{1}0)_c{}^*$ indexed with reference to the rhombohedral axes of the four individuals of the twin. Empty circlets are reciprocal-lattice nodes of crystal I, black circlets are nodes of crystal II. Concentric circles are nodes that belong to all four crystals; they are indexed in crystals I to IV, in sequence.

hkl and the six of $\overline{hkl}$. The 48 reflections (twelve from each crystal) receive the following cubic indices

$$\pm (10p - s) \cdot \pm (10q - s) \cdot \pm (10r - s),$$

where $s = 3(h + k + l)$; p, q, r stand for any one of the six permutations of h, k, l; and any one of the eight combinations of signs is permissible.

The indexed precession pattern of the net $(1\bar{1}0)_c{}^*$ (Fig. 5) shows diffraction aspect R^{**}, since rhombohedral reflections hhl are present with l odd. It is evident that the axes $[001]_c{}^*$ and $[110]_c{}^*$ are not symmetry directions in the crystals. In each of the twenty digenite twins examined by x-rays the aspect of the weighted reciprocal lattice of the twin is indeed cubic F^{***}. This fact shows that, at least within experimental

accuracy, the four individuals of the twin must have equal volumes. No twin boundaries were observed, either under the microscope or in polished sections viewed in reflected light, so that twinning is presumably of the intimate penetration type. This conclusion is confirmed by the observation that several chips broken from large twins give diffraction pat-

TABLE 2. REFLECTIONS CONTRIBUTING TO SPOT 5.15.15 ON
ROTATION PATTERN ABOUT $[001]_c$

Cubic Indices			Rhombohedral Indices										
			Crystal I			Crystal II			Crystal III			Crystal IV		
5	15	15	11	12	12	0	2	3	$\bar{2}$	$\bar{3}$	0	9	7	9
15	5	15	12	11	12	7	9	9	$\bar{3}$	$\bar{2}$	0	2	0	3
$\bar{5}$	15	15	7	9	9	$\bar{3}$	$\bar{2}$	0	2	0	3	12	11	12
$\bar{15}$	5	15	0	2	3	$\bar{2}$	$\bar{3}$	0	9	7	9	11	12	12
5	$\bar{15}$	15	2	0	3	12	11	12	7	9	9	$\bar{3}$	$\bar{2}$	0
15	$\bar{5}$	15	9	7	9	11	12	12	0	2	3	$\bar{2}$	$\bar{3}$	0
$\bar{5}$	$\bar{15}$	15	$\bar{2}$	$\bar{3}$	0	9	7	9	11	12	12	0	2	3
$\bar{15}$	$\bar{5}$	15	$\bar{3}$	$\bar{2}$	0	2	0	3	12	11	12	7	9	9

terns with identical relative intensities. (The good octahedral cleavage reported by Rahlfs for the high-temperature digenite is missing in all our specimens.)

The appearance of a pronounced pseudo-repeat $a_c' = 5.54$ Å is explained by the twinning interpretation. The reflections giving the pseudo-repeat are those with cubic indices HKL, of the form $10m \pm L$, $10n \pm L$, L, with L a multiple of 5, corresponding to two or more sets of rhombohedral reflections hkl with $h+k+l=5n$. They are the only ones to which more than one rhombohedral reflection contributes its intensity. These reflections are also the only ones for which the contributions from the sulfur atoms do not cancel one another, but have maximum positive amplitude (Table 2). We should therefore not be surprised that, with only a few exceptions, these reflections are the only ones found on the powder chart between $2\theta = 20°$ and $2\theta = 70°$. The exceptions correspond, on the precession pattern (Fig. 2), to the strongest two reflections other than the reflections of Rahlfs' pseudo-cell, namely $119_c = 223_{rh}$ ($d = 3.05$ Å) and $991_c = \overline{665}_{rh}$ ($d = 2.17$ Å). It is surprising that Buerger (1942) did not report these two reflections for the room-temperature form, since they are more intense than some of the lines which he did observe, such as his 222, which is $10.10.10_c$ referred to the large cube. Dr. Virginia Ross (priv. comm., March 1, 1957) writes: "N. Buerger's

x-ray patterns of digenite, as well as my own patterns of substituted phases that are related to digenite, exhibit lines at low temperature which alternately appear and disappear on heating and cooling."

The impossibility of finding a cubic structure and the abundance of absent reflections on "single crystal" diffraction patterns are thus explained; digenite is rhombohedral. Its aspect is R^{**}, its cell dimensions,
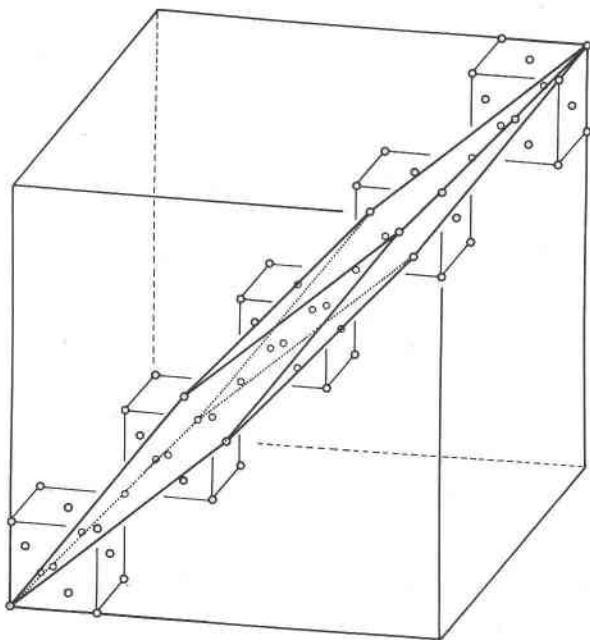

FIG. 6. Rhombohedral cell in relation to large and small cubic cells.

referred to hexagonal axes, are: $a_{\text{hex}} = a_c\sqrt{2}/10 = 3.92$, $c_{\text{hex}} = a_c\sqrt{3} = 48.0$ Å, $(c/a)_{\text{hex}} = \sqrt{150} = 12.25$, $V_{\text{hex}} = 3a_c{}^3/100$ Å^3. Since the large cubic cell contains 100 Cu$_9$S$_5$, the hexagonal cell contains 3 Cu$_9$S$_5$. The rhombohedral cell has dimensions $a_{\text{rh}} = \frac{1}{3}\sqrt{c_{\text{hex}}{}^2 + 3a_{\text{hex}}{}^2} = 16.16$ Å, $\alpha = 13°\ 56'$ (Fig. 6). It contains one Cu$_9$S$_5$.

The remarkable pseudo-symmetry of digenite, on the other hand, remains a puzzle. The $(c/a)_{\text{hex}}$ ratio stays exactly equal to $\sqrt{150}$ up to the inversion temperature; any slight deviation would lead to a splitting of powder lines, and such splitting is not observed. This means that the rhombohedral lattice can be referred to a supercell, which is *metrically cubic* throughout the stability range of the phase. The diffraction patterns, obtained from the twin, moreover, indicate cubic *symmetry*. One

is almost tempted to conclude that the crystal must be cubic. But it is not! We are dealing here with what might be called a case of high-order merohedry.[1]

A glance at *Crystal Data* (Donnay and Nowacki, 1954, p. 466) reveals that the only compound with approximately the same cell as digenite is wurtzite-15R, ZnS. The latter was studied by Frondel and Palache (1950). It occurs as *untwinned* single crystals. Its cell dimensions are $a_{hex} = 3.83$, $c_{hex} = 46.88$ Å (from kX), $c/a = 12.24$; its space group $R3m$ is obtained from x-ray results and morphological evidence. The content of the rhombohedral cell is given as Zn_5S_5, which is surprisingly different from Cu_9S_5 in view of the nearly equal cell columes. The density was not reported; it could not be determined for lack of material. We were unable to obtain any specimen of this type of ZnS.

A crystalline edifice, with the composition of the ternary compound in the Ni-Cu-Al system, remarkably similar to that of digenite, has recently been described by Bown (1956). This author was fortunate in finding single crystals of a rhombohedral species ($a = 13.53$ Å, $\alpha = 17°27'$, $V = 194.4$ Å³), on which he determined the crystal structure. In addition he describes a cubic species, which he considers a second form, with the reservation, however, that its pattern of reflections is "very nearly identical with that which would be given by a four-component multiple twin of the rhombohedral form, with the four triad axes parallel to the triads of a cube." Bown is inclined to think that the phenomenon is not one of twinning and he is going to investigate "the relation between the two forms."

CRYSTAL STRUCTURE

All attempts at growing single crystals of digenite failed, even though syntheses were made under varying conditions of temperature, rates of heating and cooling, bulk composition, etc. Only twins could be produced. Hope of obtaining single-crystal data for the determination of the crystal structure thus had to be abandoned, and our first problem was to find out how to extract, from the intensities yielded by the twinned edifice, the necessary F_{obs}-values of one individual crystal.

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[1] High-order merohedry (*mériédrie d'ordre supérieur*) is the term given (Friedel, 1926, p. 56) to a situation where the point-group symmetry of the lattice not only is higher than that of the crystal (as in the usual cases of merohedry) but is more so than necessary. For instance, a crystal with symmetry 222 normally has a lattice with point group $2/m\,2/m\,2/m$; this crystal is merohedral. If its cell had two of its edges rigorously equal, say $a = b$, and equal at all temperatures, the lattice symmetry would be $4/m\,2/m\,2/m$. The point group 222 of such an orthorhombic crystal with a tetragonal lattice would then be called a high-order merohedry. As Friedel remarks, measurements cannot *prove* the existence of high-order merohedry.

On Weissenberg and precession films, the only strong reflections are the reflections that can be indexed on the small cubic pseudo-cell; all others are too weak to be measurable. This observation determines the choice of the experimental method; only on rotation patterns taken about the 4-fold twin axis $[001]_c$ do the weak reflections become sufficiently enhanced (by the multiplicities conferred on them by the rotation and by twinning) to be measurable by visual comparison.

TABLE 3. REFLECTIONS CONTRIBUTING TO SPOT 1.9.11 ON
ROTATION PATTERN ABOUT $[001]_c$

Cubic Indices	Rhombohedral Indices			
	Crystal I	Crystal II	Crystal III	Crystal IV
1 9 11		012		
9 1 11				102
$\bar{1}$ 9 11			102	
$\bar{9}$ 1 11	012			
1 $\bar{9}$ 11	102			
9 $\bar{1}$ 11			012	
$\bar{1}$ $\bar{9}$ 11				012
$\bar{9}$ $\bar{1}$ 11		102		

The rotation pattern of the twin was first indexed with reference to the large cubic cell. The reflections with cubic indices H, K, L all multiples of 5 are due to more than one rhombohedral reflection hkl with $(h+k+l)$ divisible by 5, as shown by an example (Table 2). Such reflections cannot be used for intensity data. All other reflections can be used, for the following reasons. If $H \neq K$, as in the cubic reflection 1.9.11 for instance (Table 3), each crystal contributes the same two equivalent rhombohedral reflections; the multiplicity of the cubic reflection is therefore 8. If $H = K$ each crystal contributes one and the same reflection; and the multiplicity of the cubic reflection is 4. By dividing the measured intensity by 8, if $H \neq K$, or by 4, if $H = K$, intensities can be assigned to certain rhombohedral reflections; these intensities can be used as if they had been obtained from an isolated single crystal, provided the volumes of the component crystals in the twin are equal. The intensities were corrected for Lorentz and polarization factors.

It is convenient to discuss the crystal structure with reference to the rhombohedral axes, because they lead to a primitive cell. It is, moreover, helpful to recognize the division of the long body diagonal of this cell into five equal parts, each part representing the body diagonal of a small cube of edge 5.54 Å (Fig. 6), subsequently referred to as a cubelet.

The first fact to give a clue to the crystal structure is the steepness of the rhombohedral cell. It requires all atoms to be placed along the 3-fold axis of the cell, in positions xxx. The reasons given by Rahlfs for placing the sulfur atoms at the nodes of the face-centered cubelets are still valid; the sulfur atoms build a framework in cubic close packing. In rhombohedral positions xxx, they lie at $x=0$, $x=\pm\frac{1}{5}$, and $x=\pm\frac{2}{5}$. That these positions correspond to those chosen by Rahlfs can be seen by inspection of Fig. 6 or by applying the transposed matrix t to the cubic co-ordinates of sulfur atoms. All the sulfur atoms not listed above, which fall at the nodes of the five face-centered cubelets, belong to adjacent rhombohedral cells. For example: $\pm(.4\ .3\ .3,\ .3\ .4\ .3,\ .3\ .3\ .4)_c$ become the origins of adjacent cells $\pm(100,\ 010,\ 001)_{rh}$, etc.

The placement of copper atoms is a task quite similar to that faced by Rahlfs. Because the atoms can only occupy positions xxx, the five rhombohedral space groups compatible with diffraction aspect R^{**} can be divided into two categories on the basis of the multiplicity of the xxx position. In $R3m$ and $R3$ the position has multiplicity one; in $R\bar{3}m$, $R32$, and $R\bar{3}$, it has multiplicity two and $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$ is the only one-fold position available. We have no evidence for the absence of the center of symmetry, pyroelectric tests at liquid nitrogen temperature are negative, and we therefore proceed with the holohedral space group $R\bar{3}m$. (For the special positions xxx, space groups $R32$ and $R\bar{3}$ are undistinguishable from $R\bar{3}m$.) One copper atom is located at $x=\frac{1}{2}$, in the one-fold position; the others are found by trial and error approximately at $x=\pm0.060$, $x=\pm0.133$, $x=\pm0.250$, and $x=\pm0.350$.

This structure must be considered tentative. On those reflections that can be used in the crystal-structure determination, as explained above, the agreement between calculated and observed intensities is only moderately satisfactory. It still leaves much to be desired. The S—S distance is equal to 3.92 Å. At $x=\frac{1}{2}$ copper is octahedrally coordinated to sulfur atoms; at $x=\pm0.060$ copper lies in tetrahedral coordination, but is slightly displaced from the center of the tetrahedron toward one of its faces; at $x=\pm0.133$ copper lies in triangular coordination; at $x=\pm0.250$ and at $x=\pm0.350$, copper is in regular tetrahedral co-ordination. The Cu—S distance ranges from 2.26 Å for copper in triangular co-ordination to 2.77 Å for copper in octahedral co-ordination. If the crystal structure were of the ionic type, the formula of low-temperature digenite should be written $CuS\cdot4Cu_2S$; in which the cupric ion would correspond to the octahedrally co-ordinated copper.

The crystal structure throws light on the twin structure. If the sulfur atoms lie rigorously at the nodes of a face-centered cubic lattice, the twinning by high-order merohedry is immediately explained; the cubelet

is the cell of the twin lattice. We also note that the cell of the twin lattice is smaller than that of the crystal lattice; it is a *subcell* (or submultiple cell) of the crystal lattice. Geometrically the cell of the twin lattice could be taken to be the large cube instead of the cubelet; it would then be a *supercell* (or multiple cell) of the crystal lattice. Friedel (1926) used the supercell in his treatment of twinning; Wrinch (1952), the subcell. In the present case, the subcell is much preferable to the supercell because it possesses real structural significance; it expresses the periodicity of the sulfur atoms.

ACKNOWLEDGMENTS

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