

## LOW-CHALCOCITE AND HIGH-CHALCOCITE

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### ABSTRACT

Bristol chalcocite has been investigated by the Weissenberg method and by the de Jong-Bouman method. It is orthorhombic, diffraction symbol  $mmmAb$ ——. The  $A$ -centered cell has the following dimensions:

$$\begin{aligned}a &= 11.90 \text{ \AA} \\b &= 27.28 \\c &= 13.41\end{aligned}$$

An  $x$ -ray diffraction investigation of high-chalcocite has also been made by maintaining a Bristol chalcocite crystal above its inversion temperature of  $105^\circ \text{C}$ . This was accomplished by installing a small furnace of special construction within the Weissenberg layer-line screen, with the aid of which the crystal was maintained during the investigation at  $112^\circ \text{C}$ . The Weissenberg record shows that high-chalcocite is hexagonal, diffraction symbol  $6/mmmH6/-c-$ , and has the following cell dimensions:

$$\begin{aligned}a &= 3.89 \text{ \AA} \\c &= 6.68\end{aligned}$$

The low chalcocite cell bears a supercell relation to the high-chalcocite cell; its  $a$ ,  $b$ , and  $c$  axes are respectively 3, 4, and 2 times as long as those of the orthohexagonal high-chalcocite cell. The superstructure relationship is to be expected from inversion characteristics.

By utilizing the superstructure relationship of low-chalcocite to high-chalcocite, and the theorem that the symmetry of the superstructure must descend from the symmetry of the basic structure by suppression of repetitions, the space groups of both forms of chalcocite can be determined in spite of the fact that their diffraction symbols permit each of these crystals to have three possible space groups. The results of this reasoning are that the space group of high-chalcocite is  $H6mcm$  ( $D_{6h}^4$ ) and the space group of low-chalcocite is  $Ab2m$  ( $C_{2v}^{15}$ ).

### INTRODUCTION

Until recently the opinion has prevailed that low-chalcocite was orthorhombic and that on heating it inverted at  $91^\circ \text{C}$ . to an isometric form.<sup>1</sup> A study<sup>2</sup> of the system  $\text{Cu}_2\text{S}-\text{CuS}$  has revealed, however, that this is partially true, partially untrue. Low-chalcocite of pure  $\text{Cu}_2\text{S}$  composition indeed inverts on heating; the transformation occurs at  $105^\circ \text{C}$ . but the high form is not isometric. On the other hand, chalcocite somewhat lower in copper than ideal  $\text{Cu}_2\text{S}$  breaks up on heating into high-chalcocite and an isometric crystalline phase, digenite.<sup>3</sup> The composition of digenite has a considerable range, centering about  $\text{Cu}_9\text{S}_5$ .

<sup>1</sup> Posnjak, Eugene, Allen, E. T., and Merwin, H. E., The sulphides of copper: *Econ. Geol.*, **10**, 491-535 (1915).

<sup>2</sup> Buerger, Newton W., The chalcocite problem: *Econ. Geol.*, **36**, 19-44 (1941).

<sup>3</sup> Buerger, Newton W.,  $X$ -ray evidence for the existence of the mineral digenite,  $\text{Cu}_9\text{S}_5$ : *Am. Mineral.*, **27**, 712-716 (1942).

Evidently digenite is the same as what has been called "isometric chalcocite,"<sup>4</sup> but the symmetry of true high-chalcocite is still unknown. The only structural characteristics of low-chalcocite which are known are the cell dimensions, and there is disagreement about these. It is the chief function of this paper to report an investigation which supplies the symmetries and cells of both low-chalcocite and high-chalcocite and to point out certain relationships which exist between them. The entire investigation was carried out using untwinned fragments of crystals from the Bristol, Connecticut, chalcocite. Copper  $\alpha$ -radiation was employed throughout.

#### LOW-CHALCOCITE

The cell characteristics of low-chalcocite were first investigated by Alsen<sup>5</sup> using the powder, Laue, and rotation methods. The Laue photographs confirmed the accepted orthorhombic symmetry. Layer line spacing data from rotation photographs for the three crystallographic axes indicated the following cell:

	ratio
$a = 11.8 \text{ \AA}$	.434
$b = 27.2$	1
$c = 22.7$	.834

In connection with a more extended study of copper and silver sulfides, selenides, and tellurides, Rahlfs<sup>6</sup> reinvestigated low-chalcocite using the rotation and oscillation methods. He obtained the following cell values:

$$\begin{aligned} a &= 11.8 \text{ \AA} \\ b &= 26.9 \\ c &= 13.4 \end{aligned}$$

Rahlfs observed that his value for  $c$  differed from Alsen's value, and called attention to Alsen's difficulty in adjusting the crystal for the  $c$  axis rotation. He explained Alsen's high value as probably having been caused by rotating the crystal about [102] instead of about the  $c$  axis.

We have investigated low-chalcocite both by the equi-inclination Weissenberg method and by the equal-cone de Jong-Bouman method. The Weissenberg films include photographs of the zero, 1st, 2nd, and 3rd levels for the  $c$  axis rotation; zero and 2nd levels for the  $a$  axis rotation; and zero and 2nd levels for the  $b$  axis rotation. The de Jong films

<sup>4</sup> Schneiderhöhn, Hans, and Ramdohr, Paul, *Lehrbuch der Erzmikroskopie* II, 289 (Gebrüder Borntraeger, Berlin, 1931).

<sup>5</sup> Alsen, Nils, Ueber die Kristallstrukturen von Covellin (CuS) und Kupferglanz (Cu<sub>2</sub>S): *Geol. För. I Stockholm Förh.*, 53, 117-118 (1931).

<sup>6</sup> Rahlfs, Paul, Ueber die kubischen Hochtemperaturmodifikationen der Sulfide, Selenide und Telluride des Silbers und des einwertigen Kupfers: *Zeits. phys. Chem. (B)*, 31, especially p. 193 (1936).

include the zero, 1st, 2nd, 3rd, 4th, 5th, and 6th levels for the  $c$  axis rotation. Simple rotating crystal photographs were also made for rotations about each of the three crystallographic axes.

The zero level  $c$  axis photographs are plainly pseudo-hexagonal, Fig. 1. The hexagonaloid character is dimensionally very close.



FIG. 1. de Jong-Bouman photograph, low-chalcocite,  $c$  axis rotation, zero level,  $\mu = 45^\circ$ , Cu  $K\alpha$  radiation filtered through nickel foil. Note pseudo-hexagonal distribution of strongest spots, and overall symmetry  $C_{2v}$ . (A few spots without symmetrically related companions are due to a tiny satellitic twin fragment on one side of the main crystal.)

The level photographs plainly show the crystal to have diffraction symmetry  $mmm$ . The diffraction symbol  $mmmAb$  — is required by the missing reciprocal lattice points. This permits the space group of low-chalcocite to be either  $Abmm$ ,  $Ab2m$ , or  $Abm2$ . (The last two are different orientations of the same space group,  $C_{2v}^{15}$ , both of which are consistent with the diffraction data.) It will be shown later that the correct space group is probably  $Ab2m$ .

The cell dimensions of low-chalcocite are (accuracy, about 1%):

	ratio
$a = 11.90 \text{ \AA}$	.437
$b = 27.28$	1
$c = 13.41$	.492

For a density<sup>1</sup> of 5.8 g./c.c., these dimensions call for 96 Cu<sub>2</sub>S per cell.

It will be noted that our cell dimensions are in substantial agreement with Rahlf's.

#### HIGH-CHALCOCITE

In order to investigate the symmetry and cell of high-chalcocite, a furnace was devised<sup>7</sup> for maintaining the crystal at an elevated temperature in a Weissenberg apparatus. This heating unit is similar to that used in the controlled-temperature powder camera,<sup>8</sup> but is so arranged that it is contained within the layer-line screen of the Weissenberg apparatus. For investigating chalcocite, the crystal was maintained at 112°C. (i.e., above the inversion temperature, 105°C.).

An untwinned fragment of Bristol chalcocite was first summarily investigated at room temperature by means of a  $c$  axis rotation photograph and a  $c$  axis zero-layer Weissenberg photograph. The temperature of the crystal was then raised to 112°C., and the following photographs were taken for  $c$  axis rotations while the crystal was maintained at this temperature: simple rotation photograph and equi-inclination Weissenberg resolutions of the zero, 1st, 2nd, and 3rd layers.

The relation between the  $c$  axis photographs taken for the crystal held at room temperature and at 112°C. is shown in Fig. 2. When the crystal is heated through the inversion, the rotation photographs show that the  $c$  axis translation becomes halved and the Weissenberg photographs show that the symmetry changes from pseudohexagonal orthorhombic to true hexagonal. This is accompanied by a reduction in the other cell dimensions and consequent vanishing of many of the spots on the zero-level Weissenberg photographs, Fig. 3.

The crystal was also investigated, while being maintained at 112°C., with the aid of rotation photographs and zero and 2nd level equi-inclination Weissenberg photographs for rotations about the  $a$  axis and about the  $[\bar{1}10]$  axis (i.e., the orthohexagonal  $b$  axis).

<sup>7</sup> Buerger, Newton W., Weissenberg controlled-temperature technique. *Program and Abstracts*, Twenty-second Annual Meeting, Mineralogical Society of America, December 29-31 (1941) pages [8]-[9].

<sup>8</sup> Buerger, M. J., Buerger, Newton W., and Chesley, Frank G., Apparatus for making x-ray powder photographs at controlled, elevated temperatures: *Am. Mineral.*, **28**, 285-302 (1943).

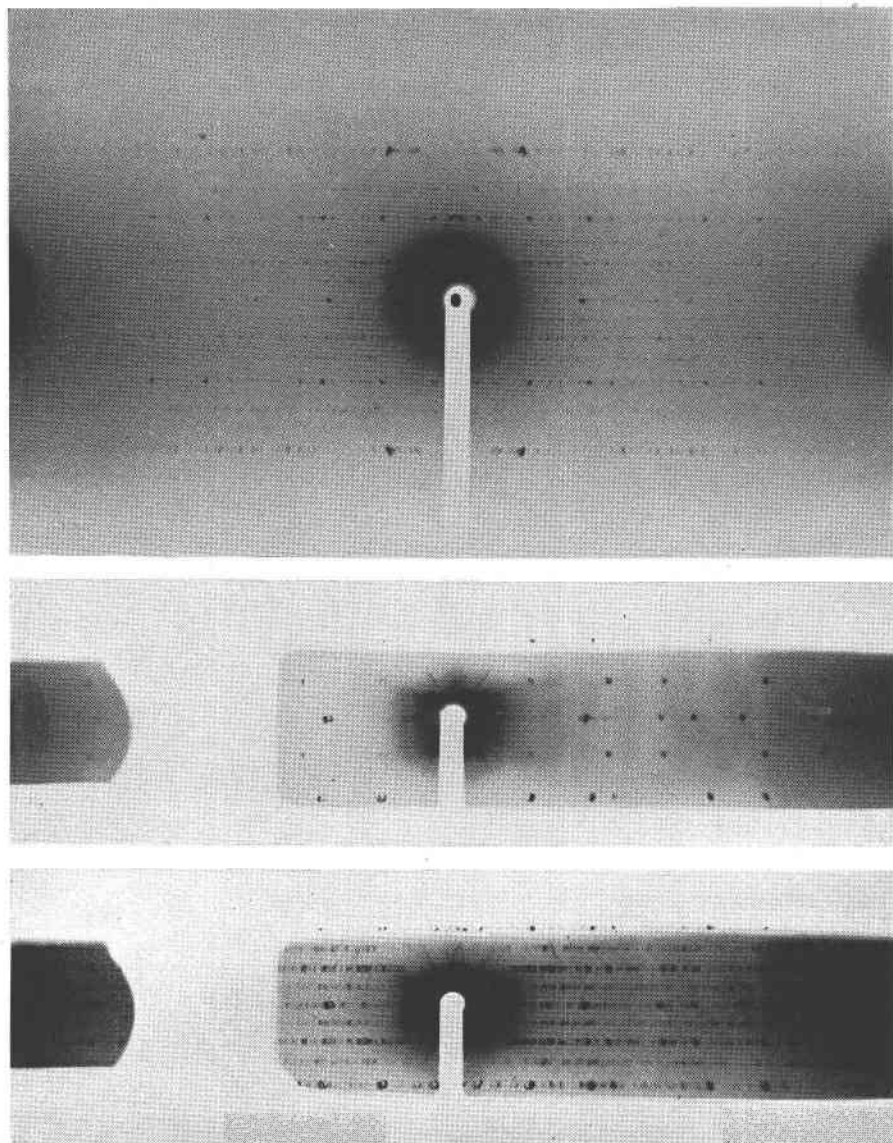


FIG. 2. Rotating-crystal photographs of chalcocite for  $c$  axis rotation, Cu  $K\alpha$  radiation filtered through nickel foil.

Upper photograph: low-chalcocite crystal.

Middle photograph: high-chalcocite crystal resulting from heating low-chalcocite crystal to  $112^\circ\text{C}$ .

Lower photograph: low-chalcocite resulting from cooling the high-chalcocite crystal of the middle photograph to room temperature.

Note that the layer line spacing in the middle photograph is about twice that of the upper photograph, indicating a  $c$  translation of about half that for the upper photograph. Note, also, that (making allowances for differences in apparatus which affect recording range and x-ray beam divergence) the upper and lower photographs are substantially the same, indicating that the transformation from low- to high-chalcocite is reversible.

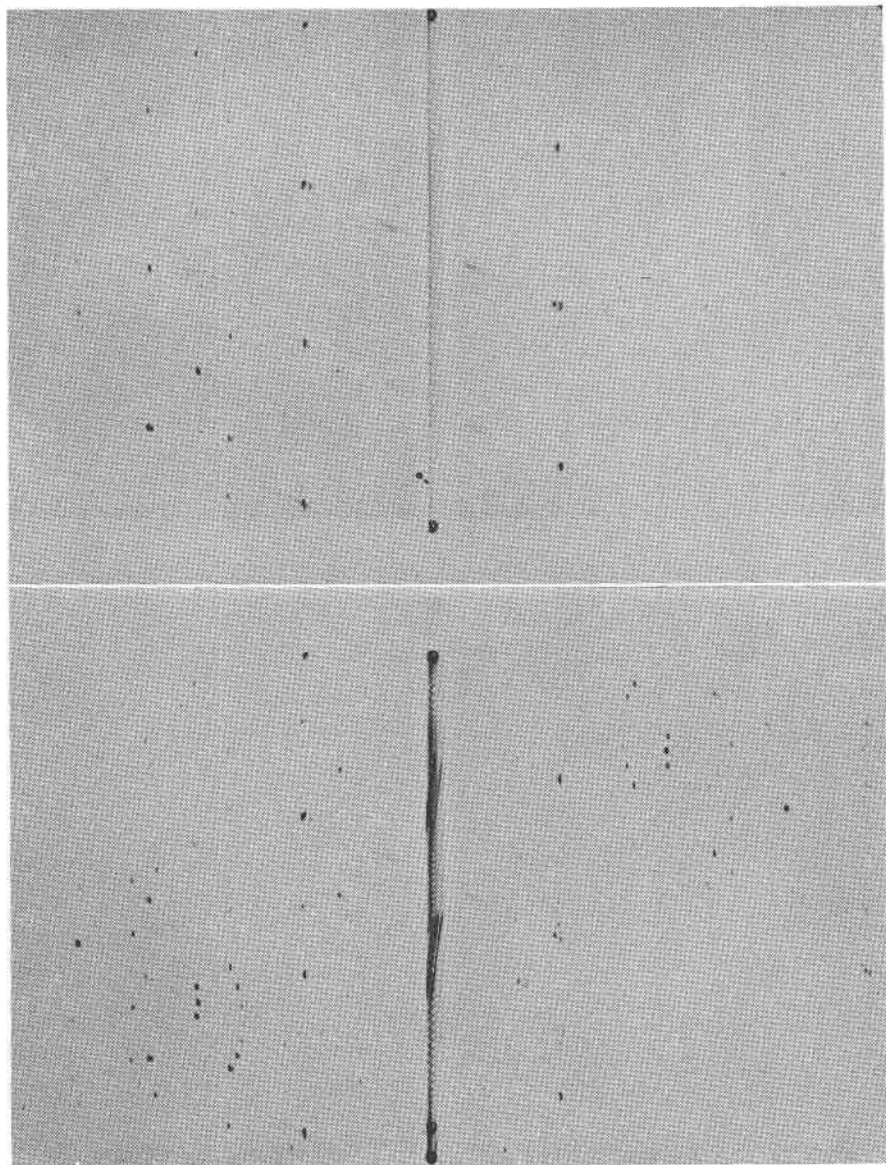


Fig. 3. Weissenberg photographs of chalcocite,  $c$  axis, zero layer,  $\text{Cu K}\alpha$  radiation filtered through nickel foil. Left photograph: original low-chalcocite crystal.

Right photograph: high-chalcocite crystal resulting from heating low-chalcocite crystal to  $112^\circ\text{C}$ . Note that the left photograph has all the spots of the right photograph plus some additional ones due to the superstructure. (A few weak spots are due to a satellitic fragment on the main crystal.)

The Weissenberg photographs of high-chalcocite reveal that its diffraction symmetry is  $6/mmm$ . Missing reciprocal lattice points require the diffraction symbol  $6/mmmH-/-c-$ . This permits the space group of high-chalcocite to be either  $H6/mcm$ ,  $H6cm$ , or  $H\bar{6}c2$ . It will be shown subsequently that the correct space group is probably  $H6/mcm$ .

The unit cell of high-chalcocite has the following dimensions (accuracy, about 1%):

	ratio
$a = 3.89\text{\AA}$	1
$c = 6.68$	1.717

According to Sahmen and Tammann,<sup>9</sup> the specific volumes of chalcocite above and below the inversion do not differ by more than .00012 c.c./gm.; so that no appreciable error is made in taking the density of high-chalcocite as 5.8 g./c.c. For this density, the hexagonal cell contains  $2\text{Cu}_2\text{S}$ .

#### RELATIONSHIPS BETWEEN HIGH-CHALCOCITE AND LOW-CHALCOCITE

*Dimensional Relationships.*—It is known<sup>1,2</sup> that low-chalcocite and high-chalcocite are connected by a rapid transformation. This calls for small structural displacements at the inversion and consequently it is not surprising that, as has been briefly indicated in the last section, the lattice periods of the two forms of chalcocite are related in a simple fashion. The relationship is graphically illustrated in Fig. 4.

The dimensional relationships between the two forms of chalcocite can be represented in several ways. Indicating properties of the high form by the subscript  $H$  and of the low form by the subscript  $L$ , and using vector notation, the lengths and directions of the cell edges of the two forms of chalcocite are very approximately related as follows:

$$\begin{aligned} \mathbf{a}_L &= 3\mathbf{a}_{1H} + 3\mathbf{a}_{2H} \\ \mathbf{b}_L &= -4\mathbf{a}_{1H} + 4\mathbf{a}_{2H} \\ \mathbf{c}_L &= 2\mathbf{c}_H \end{aligned}$$

This can be compactly represented by the matrix of these equations:

Low-chalcocite (doubly primitive,  $A$ -centered)  
from

High-chalcocite (primitive hexagonal)

$$\begin{vmatrix} 3 & 3 & 0 \\ \bar{4} & 4 & 0 \\ 0 & 0 & 2 \end{vmatrix}, \text{ modulus } 48.$$

<sup>9</sup> Sahmen, R. v., and Tammann, G., Über das Auffinden von Umwandlungspunkten mit einem selbstregistrierenden Dilatographen: *Ann. der Phys.* (4), **10**, 881 (1903).

The 48-fold multiplicity of the low-chalcocite supercell is somewhat misleading because for convenience the orthorhombic prismatic lattice is described by an *A*-centered, and consequently, doubly-primitive, cell.

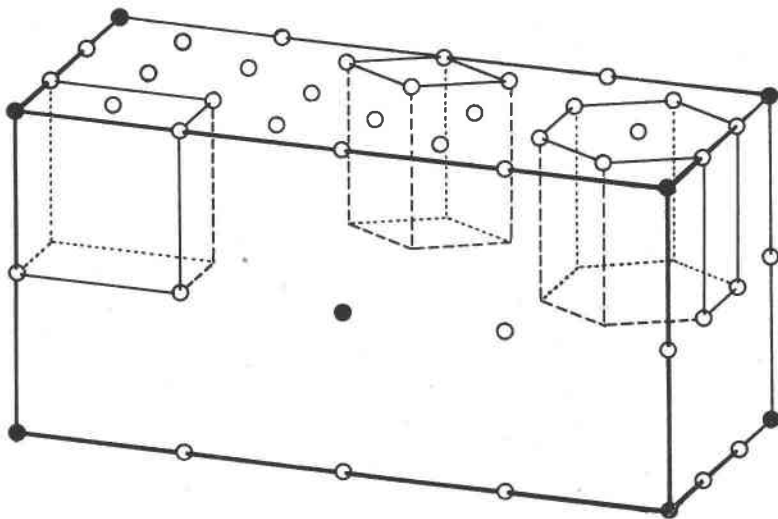


FIG. 4. Relation between the low-chalcocite cell and various cells chosen from the high-chalcocite lattice. The black dots are the lattice points of low-chalcocite, and the large block represents its *A*-centered cell. The open dots are lattice points of high-chalcocite. Three kinds of high-chalcocite cells are outlined; from left to right these are: orthohexagonal unit cell, primitive hexagonal unit cell, and hexagon cell.

The multiplicity of the primitive orthorhombic low-chalcocite supercell is only 24.

The relationship between the cells of the two forms of chalcocite can perhaps better be appreciated by referring the hexagonal, high-chalcocite cell to orthohexagonal axes. The cells of the two forms then compare as follows:

<i>Low-chalcocite</i> , <i>A</i> -centered, orthorhombic cell	<i>High-chalcocite</i> , orthohexagonal cell
$a = 11.90 \text{ \AA}$	$3.89 \text{ \AA} (\times 3 = 11.67 \text{ \AA})$
$b = 27.28$	$6.79 (\times 4 = 27.16 \text{ \AA})$
$c = 13.49$	$6.68 (\times 2 = 13.36 \text{ \AA})$
cell contents $96 \text{ Cu}_2\text{S}$	$4 \text{ Cu}_2\text{S} (\times 24 = 96 \text{ Cu}_2\text{S})$

Thus, the transformation from high-chalcocite to low-chalcocite is accompanied by multiplication of the lengths of the identity periods in



the three orthogonal directions, such that the  $a$  axis is tripled, the  $b$  axis is quadrupled, and the  $c$  axis is doubled. This relationship can be compactly represented by the matrix:

$$\begin{array}{c} \text{Low-chalcocite (doubly primitive, } A\text{-centered)} \\ \text{from} \\ \text{High-chalcocite (doubly primitive, orthohexagonal)} \\ \left\| \begin{array}{ccc} 3 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 2 \end{array} \right\|, \text{ modulus } 24. \end{array}$$

*Symmetry Relationships.*—Valuable information can be obtained by comparing the distribution of symmetry in the two chalcocite modifications. Since the orthohexagonal high-chalcocite cell is oriented parallel to the orthorhombic low-chalcocite cell, the symmetry symbols of the high-chalcocite will be written, for purposes of this comparison, in the sequence standard for orthorhombic crystals.

The diffraction symbols and the possible space groups they may indicate, for low- and high-chalcocite, are shown in the following tabulation:

Diffraction Symbol	High-Chalcocite $m m m C - c -$	Low-Chalcocite $m m m A b - -$
Included	$C m c m$	$A b m m$
Space Groups	$C m c 6$ $C 2 c \bar{6}$	$A b 2 m$ $A b m 2$

Now, it was demonstrated in the last section that a supercell dimensional relation exists between the two forms of chalcocite. It is extremely likely that superstructural symmetry relations also exist between them. The most fundamental theorem governing the symmetry of a superstructure is that it must be derivable from the symmetry of the basic structure by suppression of certain elementary repetitions.<sup>10</sup> This requires that one or more of the space groups possible for low-chalcocite must be derivatives of one or more of the space groups possible for high-chalcocite. The above table indicates that, so far as  $x$ -ray data are concerned, three possible low-chalcocite space groups are possible derivatives of three possible high-chalcocite space groups, giving nine possible derivations.

Whether a derivation is possible or not can be conveniently studied by utilizing the complete Mauguin space group symbols<sup>11</sup> instead of the usual international abbreviated symbols. In the accompanying table, the complete Mauguin symbol of the high-chalcocite space group is placed above the complete Mauguin symbol for the low-chalcocite space group

<sup>10</sup> This will be discussed in greater detail elsewhere.

<sup>11</sup> Buerger, M. J., *X-ray Crystallography*, table 7, pages 84–89, second column.

for each of the nine possible derivations. The arrow indicates the direction of the derivation. In this tabulation, an  $x$  is placed below an indicated derivation which is impossible.<sup>11</sup>

Note that only one possible derivation of low-chalcocite symmetry from high-chalcocite symmetry is entirely without  $x$ 's, indicating that this entire low-chalcocite symmetry can be derived from the high-chalcocite symmetry. It is difficult to avoid the conclusion that these two space groups are the correct ones for low-chalcocite and high-chalcocite, respectively.

Transforming these symbols to abbreviated international form, and to normal sequence in the hexagonal case, the space groups for these crystals are as follows:

High-chalcocite	$H6/mcm$	$(D_{6h}^4)$
Low-chalcocite	$Ab2m$	$(C_{2v}^{16})$

If this analysis is correct, it is important to note that one of its consequences is that the crystal class of low-chalcocite is not holohedral, but hemimorphic (pyramidal)  $m2m$ .

$\begin{array}{c} \left  \begin{array}{c} C \frac{2}{m} \frac{2}{c} \frac{6_3}{m} \\ \downarrow A \frac{2}{b} \frac{2}{m} \frac{2}{m} \\ x \quad x \end{array} \right. \end{array}$	$\begin{array}{c} \left  \begin{array}{c} C \quad m \quad c \quad 6_3 \\ \downarrow A \frac{2}{b} \frac{2}{m} \frac{2}{m} \\ x \quad x \quad x \end{array} \right. \end{array}$	$\left  \begin{array}{c} C \quad 2 \quad c \quad \bar{6} \\ \downarrow A \frac{2}{b} \frac{2}{m} \frac{2}{m} \\ x \quad x \quad x \end{array} \right.$
$\left  \begin{array}{c} C \frac{2}{m} \frac{2}{c} \frac{6_3}{m} \\ \downarrow A \quad b \quad 2 \quad m \\ x \quad x \end{array} \right.$	$\left  \begin{array}{c} C \quad m \quad c \quad 6_3 \\ \downarrow A \quad b \quad 2 \quad m \\ x \quad x \end{array} \right.$	$\left  \begin{array}{c} C \quad 2 \quad c \quad \bar{6} \\ \downarrow A \quad b \quad 2 \quad m \\ x \quad x \quad x \end{array} \right.$
$\left  \begin{array}{c} C \frac{2}{m} \frac{2}{c} \frac{6_3}{m} \\ \downarrow A \quad b \quad m \quad 2 \\ x \quad x \end{array} \right.$	$\left  \begin{array}{c} C \quad m \quad c \quad 6_3 \\ \downarrow A \quad b \quad m \quad 2 \\ x \quad x \end{array} \right.$	$\left  \begin{array}{c} C \quad 2 \quad c \quad \bar{6} \\ \downarrow A \quad b \quad m \quad 2 \\ x \quad x \quad x \end{array} \right.$

#### CONCLUSION

This paper should not be concluded without pointing out how correctly Groth<sup>12</sup> had critically appraised the relationship between low- and high-chalcocite. He contended that a transformation from orthorhombic low-chalcocite to the supposed isometric high-chalcocite ought to involve important volume changes, which Sahmen and Tammann<sup>9</sup> had

<sup>12</sup> Groth, P., *Chemische Kristallographie*, **1**, 135 (1906).

not found in the region of the transformation. From this Groth concluded that the resistance changes which occurred when heating orthorhombic chalcocite through the region near 100°C. and noted by Hittorff<sup>13</sup> and Mönch<sup>14</sup> were related to some other kind of transition, not to a transformation from orthorhombic chalcocite to "isometric chalcocite." We now know that this view was correct; that orthorhombic chalcocite does not invert to "isometric chalcocite" (i.e., digenite). As Groth surmised, there is a somewhat different relation occurring at the true chalcocite transition, namely, the two structures are very similar, the transition involving no great volume changes, but merely a slight shifting of the atomic arrangement such that the low-form assumes a superstructure based upon the basic structure of the high-form.

<sup>13</sup> Hittorff, Ueber das electrische Leitungsvermögen des Schwefelsilbers und Halbschwefelkupfers: *Ann. Phys. u. Chem.*, **84**, 1-28 (1851).

<sup>14</sup> Mönch, Willy, Ueber die elektrische Leitfähigkeit von Kupfersulfür, Silber-, Blei-, und schwarzem Quecksilbersulfid: *Neues Jahrb. Min.*, etc., B. B. **20**, 365-435 (1905).