

### UNIT CELL AND SPACE GROUP OF CHALCOCITE, $Cu_2S$

In 1930, when doing X-ray work in the Mineralogical Laboratory in Cambridge, I took a number of oscillation photographs of chalcocite from Cornwall. Axes of rotation were the 3 crystallographic axes. From the photographs the following dimensions of the unit cell were derived:

$$a_o = 11.8 \text{ \AA} \quad b_o = 27.0 \text{ \AA} \quad c_o = 13.4 \text{ \AA}.$$

These values are not very exact; they may be uncertain by about 0.1 Å. They are in close agreement with a set of values which has been published in the meantime.<sup>1</sup> Because of the very large number of atoms which must be contained in this cell I did not think it possible to determine the structure from the photographs; in any case such a determination would be an extremely laborious task; and so I did not publish any account on my work chalcocite. Reviewing my old photographs I find that a fairly reliable determination of the space group is possible. The interpretation of the photographs was done by the graphical method worked out by J. D. Bernal.<sup>2</sup> Because of the large size of the unit cell a unique interpretation was possible only for part of the spots in each photograph. Even so I obtained a list of about 200 different sets of indices which may be regarded as well established, many of them being represented by several spots. In all of these observed sets of indices  $hkl$  the sum  $k+l$  is even, that is:  $k$  and  $l$  are either both even or both odd; in other words: *hkl is halved if  $k+l$  is odd.* This seems to be the only kind of abnormal spacings. The only space group in accordance herewith is  $C_{2v}^{14} - Amm$ . Interchanging the axes  $a$  and  $c$  also  $C_{2v}^{11} - Cmm$ .  $Q^6 - C222$  and  $Q_h^{19} - Cmmm$  are possible. As no faces indicating a lower symmetry than the orthorhombic holohedral have been observed on crystals of chalcocite, all these space groups but the last one are improbable. *The space group of chalcocite is therefore probably  $Q_h^{19} - Cmmm$ .* To be in accordance with the space group notation here adopted we have, as mentioned, to interchange the axes  $a$  and  $c$  in the usual orientation of the chalcocite crystals.

As to the number of atoms in the unit cell neither the cell dimensions nor the specific gravity of chalcocite are known with sufficient accuracy to give a unique result. Using the above cell dimensions and the specific gravity 5.8 we obtain about 93  $Cu_2S$  in the unit cell. It is, however, highly probable that the correct number is 96. This is supported by several facts. 96  $Cu_2S$  in the unit cell gives a calculated density of 5.97, which is the value found for cubic  $Cu_2S$  by Tom. Barth.<sup>3</sup> In other words: the cubic cell, which contains 4  $Cu_2S$ , is very exactly 1/24 the volume of the orthorhombic cell. It might be assumed that the orthorhombic cell would be built up of 24 more or less distorted cubic cells, but this does not seem to be the case. It is true that the intensities of

<sup>1</sup> P. Rahlfs, Z. physik. Chem. (B) 31, 157, 1936.

<sup>2</sup> J. D. Bernal, On the interpretation of X-ray, single crystal, rotation photographs. Proc. Roy Soc. (A) 113, 117, 1927.

<sup>3</sup> Tom. Barth, Die reguläre Kristallart von Kupferglanz. Centralblatt f. Min. etc., A, 1926, p. 285.

the spots in the oscillation photographs indicate a fairly distinct pseudo cell which is  $1/24$  the volume of the orthorhombic unit cell, but its shape is very far from cubic. This pseudo cell is indicated by the relatively very high intensities of spots with indices like 084, 086, 344, 346, 3 12 0, 3 12 2, 3 12 4. These indices are of the form  $3n$ ,  $4n$ ,  $2n$ , and the pseudo cell thus has the dimensions  $\frac{1}{3}a_0$ ,  $\frac{1}{4}b_0$ ,  $\frac{1}{2}c_0$ , or 3.94 Å, 6.75 Å, 6.70 Å. The pseudo cell is therefore pseudo-tetragonal, and also pseudo-hexagonal. (In accordance with what has been said above the product  $3.94 \text{ Å} \times 6.75 \text{ Å} \times 6.70 \text{ Å}$  is very nearly equal to  $(5.59 \text{ Å})^3$ , which is the volume of the unit cell of cubic  $\text{Cu}_2\text{S}$ .) — The general positions of equivalent points in the space group  $Q_h^{19} - Cmmm$  are sixteen-fold. This is an additional indication that the real number of "molecules"  $\text{Cu}_2\text{S}$  in the unit cell is 96 and not a number in the neighbourhood of 96, for 192 and 96 positions are readily built up of sets of 16.  $12 + 6$  sets of 16 will be needed, and the number of parameters to be fixed to determine the structure is probably  $(12 + 6) \times 3$ , or 54.

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#### NOTE ON THE METAMORPHIC DIFFERENTIATION OF SOLID ROCKS

This note should be considered as a supplement to my article in this journal 24 p. 98—111.

The activity of the given mineral usually varies with the kind and composition of the surrounding minerals (the variation of the activity with  $Z$ ) even if the composition and the size of the given mineral and the  $P$ ,  $T$  are constant. This is because of the influence of the surrounding phases on the surface tension of the considered phase. Thus, in a homogeneous rock consisting of chemically compatible minerals it may happen that the activities of the assemblage decrease if special minerals cluster concretionary together. During the metamorphism there will therefore exist activity gradients in a homogeneous rock that try to differentiate the rock by dispersion of some minerals at some places, migration of the dispersed elements towards places of lower activities and consolidation there. The variation of the activity of a mineral with the surrounding phases is thus — along with the variation of the activity with the pressure,  $P$ , and the size of mineral,  $Y$  — the most important factor to consider when treating the metamorphic differentiation theoretically. In this way I explain the occurrence of concretions of many mineral assemblages as for instance calcite in slate, chert in chalk, quartz and small pegmatite veins in gneisses, epidote, quartz and calcite in low grade amphibolites and so on. During the growth of the concretion which commonly consists of minerals containing the element with the greatest power of diffusion in the rock, the other minerals must be enriched in a zone along the boundary of the concretion.

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