

## The crystal structures of low chalcocite and djurleite\*

Howard T. Evans, Jr.

U.S. Geological Survey, National Center 959, Reston, Virginia 22092, USA

Received: March 19, 1979

**Abstract.** Low chalcocite is monoclinic, space group  $P2_1/c$ , with a unit cell having  $a = 15.246(4)$  Å,  $b = 11.884(2)$  Å,  $c = 13.494(3)$  Å,  $\beta = 116.35(1)^\circ$ , and containing  $48 \text{ Cu}_2\text{S}$ . Its structure was solved by the symbolic addition method, using 5155 independent intensity data measured with  $\text{MoK}\alpha$  radiation on an automatic diffractometer. Refinement in anisotropic mode led to  $R = 0.086$ . The structure is based on hexagonal-close-packed framework of sulfur atoms, with copper atoms occupying mainly triangular interstices. Of the 24 different copper atoms, 21 form triangular  $\text{CuS}_3$  groups, and one is in a distorted  $\text{CuS}_4$  tetrahedron.

Djurleite is monoclinic, space group  $P2_1/n$ , with a unit cell having  $a = 26.897(6)$  Å,  $b = 15.745(3)$  Å,  $c = 13.565(3)$  Å,  $\beta = 90.13(3)^\circ$ , and containing  $8 \text{ Cu}_3\text{S}_{16}$ . The structure was solved by extending the known substructure phases by the symbolic addition procedure, using 5686 independent intensity data measured with  $\text{MoK}\alpha$  radiation. Refinement converged at  $R = 0.116$ . The structure is similar in general to the low chalcocite structure, but of the 62 different copper atoms, 52 form triangular groups, 9 form distorted tetrahedral groups, and one is in unique linear twofold coordination.

Both structures are derived from the high chalcocite structure ( $P6_3/mmc$ ,  $a = 3.96$  Å,  $c = 6.72$  Å, cell content =  $2 \text{ Cu}_2\text{S}$ ) which forms a substructure corresponding to the hexagonal-close-packed sulfur framework, but the details of the copper arrangement are entirely different in the two phases. The average Cu–S bond length in the  $\text{CuS}_3$  triangles is 2.32 Å in low chalcocite and 2.29 Å in djurleite. The overall average Cu–S distance in the tetrahedra is 2.48 Å, but varies from 2.22 to 2.91 Å. Each copper atom has from 2 to 8 other copper atom neighbors less than 3.0 Å distant, varying up from 2.45 Å through a maximum clustering at about 2.78 Å. Cu–Cu bonding interaction is probably significant but is not clearly understood.

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\* Dedicated to Prof. W. Nowacki on occasion of his 70th birthday

### Introduction

Several major detailed studies of the Cu–S system have been published (Roseboom, 1966; Rau, 1967; Cook, 1972; Potter, 1977), all of which show the existence of two phases  $\text{Cu}_x\text{S}$  at room temperature with  $x$  close to 2. The stoichiometric phase  $\text{Cu}_2\text{S}$  has long been known as chalcocite, a supergene or hypogene ore mineral of copper. The existence of the compositionally close-lying phase having  $x = 1.96$  was discovered in an X-ray study of the Cu–S system by Djurle (1958), and soon became recognized as a mineral which was named in his honor (Roseboom, 1962; Morimoto, 1962). Mathieu and Rickert (1972), and Potter (1977), in careful electrochemical studies, showed that (low) chalcocite at room temperature has a very narrow homogeneity range, in which  $x$  lies between 1.997 and 2.000 ( $\pm 0.002$ ). The range is considerably broader for djurleite, as  $x$  ranges between 1.934 to 1.965  $\pm 0.002$ . The low-temperature form of chalcocite, commonly designated “low chalcocite”, and djurleite both revert on heating to the disordered hexagonal phase called “high chalcocite”, the former at 103.5° C, the latter at 93° C.

Both low chalcocite and djurleite are very common species, often intermixed or intergrown. Many specimens in museums and study collections labelled “chalcocite” may actually be primarily djurleite. A comprehensive study of the crystal habits of the two minerals has not yet been made, but the author’s experience suggests that the elongated prismatic habit of crystals from Bristol, Connecticut is characteristic of low chalcocite, and that the flat, hexagonal, platy habit bounded by prisms that is common at Redruth, Cornwall, is characteristic of djurleite. Their physical and optical properties are practically identical. Thus, the only certain method to distinguish the two is X-ray diffraction (Roseboom, 1966).

The structures of both low chalcocite and djurleite are based on a hexagonal-close-packed framework of sulfur atoms, with the copper atoms arranged in a complex way in the interstices. At about 100° C the copper atoms become highly disordered, virtually “fluid”, with the transformation to high chalcocite, for which the crystallography, as Ueda (1949) first showed, is simply that of the sulfur framework itself. The high mobility of copper in this phase is associated with unusually high ionic conductivity, as shown by Hirahara (1951). When the copper atoms “freeze” on cooling in a sharp, first-order transition, they become fixed in either the low chalcocite or the djurleite arrangement, presumably depending on the local Cu/S proportions at the point of nucleation, although Putnis (1976) claimed that one or the other may appear at random at stoichiometric composition. Knowledge of the details of the copper arrangement in the low temperature phases has naturally been much desired as new aspects of the complex Cu–S system have been discovered. Both structures have now been solved by the author in this laboratory, and their structure analyses and the resulting

