

The crystal structures of low chalcocite and djurleite*

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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 CuS_3 groups, and one is in a distorted 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 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.

* 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 Cu_xS at room temperature with x close to 2. The stoichiometric phase Cu_2S 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 (± 0.002). The range is considerably broader for djurleite, as x ranges between 1.934 to 1.965 ± 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

detailed atomic arrangements are described in this paper. Preliminary notices of these findings have been published previously (Evans, 1971; Evans, 1979).

Previous crystallographic studies

The proper pseudo-orthorhombic cell of low chalcocite was first determined by Rahlfs (1936). A detailed analysis of the crystallography of this phase was then reported by Buerger and Buerger (1944), who established an A-centered orthorhombic cell with $a = 11.92 \text{ \AA}$, $b = 27.84 \text{ \AA}$ and $c = 13.44 \text{ \AA}$, containing $96 \text{ Cu}_2\text{S}$. Assuming that the crystal is orthorhombic, they showed that the space group $A b 2m$ is the only one compatible with the hexagonal unit cell of high chalcocite, from which it is most probably derived as a superstructure produced by small atomic displacements. However, the nature of this superstructure has remained hidden until the present study.

The first insight into the structure of high chalcocite was given by Ueda (1949), who showed that an approximate explanation of the observed X-ray intensities is obtained on the basis of two sulfur atoms in the cell in hexagonal closest packing, with no regard to the copper atoms. It became clear that this hexagonal-close-packed sulfur framework prevails also in low chalcocite, associated with the pseudohexagonal character observed by Buerger and Buerger (1944). Eventually, by careful electron density study of the high chalcocite cell, Wuensch and Buerger (1963) and also Koto and Morimoto (1965) found that the sulfur framework is sharply delineated, but that the copper atoms are highly disordered, being smeared out through the interstices, with some concentration at triangular, tetrahedral and linear coordination sites.

As mentioned above, djurleite was first recognized in an X-ray study by Djurle (1958), who assigned to it an orthorhombic cell in space group $Pmnm$ containing $128 \text{ Cu}_x\text{S}$ where $x = 1.96$. A detailed study of the crystallography of this phase, which is complicated by extensive twinning (Takeda, Donnay and Appleman, 1967), was made by Takeda, Donnay, Roseboom and Appleman (1967). They showed clearly how the superstructure relationship between high and low chalcocite extends also to djurleite, which has a pseudohexagonal character even stronger than that of low chalcocite. These authors listed an orthorhombic cell like that of Djurle (1958), but expressed the strong feeling that the phase may actually be monoclinic in space group $P 2_1/n$. The present author had the privilege of examining their precession photographs, from which it was possible to reach this conclusion unequivocally. With the later discovery of untwinned crystals, the fact was dramatically confirmed.

Crystallographic metrics of chalcocite and djurleite

The unit cell dimensions of chalcocite and djurleite were determined by means of least squares analysis of X-ray powder data obtained from the Hägg-Guinier focussing camera. The method and resulting powder data have been presented by Potter and Evans (1976). The unit cells obtained are given in Table 1, which is analogous to Table 2 of Takeda, Donnay, Roseboom and Appleman (1967). For low chalcocite, a crystal from Bristol, Connecticut was used for the powder run and all subsequent single crystal work. The composition is assumed to be essentially invariant at Cu_2S . The full set of single crystal intensity data were available to enable Potter and Evans to index the powder pattern unambiguously on the monoclinic cell. This was not the case for djurleite at that time, so they assumed an orthorhombic cell. Also, the sample of djurleite from the Ozark Lead Co. mine at Sweetwater, Missouri, that was used for the powder pattern (and also the subsequent

Table 1. Unit cells of high chalcocite, low chalcocite, and djurleite

Parameter	High chalcocite ^a	Low chalcocite		Djurleite
		ps.-ortho. ^b	monoclinic	
Space group	$P6_3/mmc$	$A2_1/c$ 11	$P2_1/c$	$P2_1/n$
a , Å	$\begin{cases} a_{cch}^c \\ 3.961(4) \end{cases}$	$\begin{cases} a_{cco}^c \sim 3 a_{cch} \\ 11.884(2) \end{cases}$	$\begin{cases} a_{ccm}^c = [0, \frac{1}{2}, \frac{1}{2}]_{cco} \\ 15.246(4) \end{cases}$	$\begin{cases} a_{dj}^c \sim 4 c_{cch} \\ 26.897(6) \end{cases}$
b , Å	$\begin{cases} b_{cch} \\ 6.861(6) \end{cases}$	$\begin{cases} b_{cco} \sim 4 b_{cch} \\ 27.324(4) \end{cases}$	$\begin{cases} b_{ccm} = a_{cco} \\ 11.884(2) \end{cases}$	$\begin{cases} b_{dj}^c \sim 4 a_{cch} \\ 15.745(3) \end{cases}$
c , Å	$\begin{cases} c_{cch} \\ 6.722(7) \end{cases}$	$\begin{cases} c_{cco} \sim 2 c_{cch} \\ 13.494(3) \end{cases}$	$\begin{cases} c_{ccm} = c_{cco} \\ 13.494(3) \end{cases}$	$\begin{cases} c_{dj} \sim 2 b_{cch} \\ 13.465(3) \end{cases}$
β	—	90.08(1)	116.35(1)	90.13(2)
V , Å ³	182.7	4382(2)	2190(1)	5744(2)
Cell contents	2 Cu ₂ S	96 Cu ₂ S	48 Cu ₂ S	8 Cu ₃₁ S ₁₆
D_x , gm/cm ³	5.785		5.789	5.740

^a Orthohexagonal cell at 152°C according to Djurle (1958)

^b Setting of Buerger and Buerger (1944)

^c Subscripts: *cch* = high chalcocite; *cco* = low chalcocite, pseudo-orthorhombic setting; *ccm* = low chalcocite, primitive monoclinic setting; *dj* = djurleite

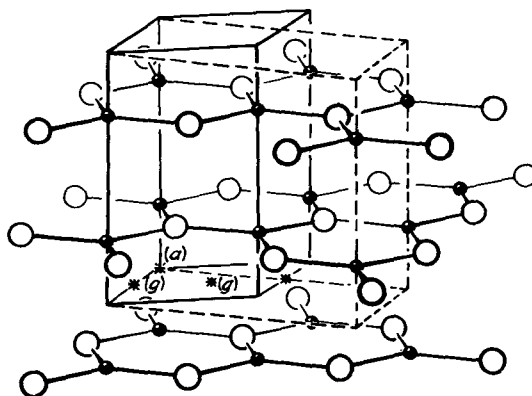


Fig. 1. The partial structure of high chalcocite, showing the characteristic CuS layers. Centers of symmetry are indicated by (a) and (g). Dashed lines show orthohexagonal unit cell

single crystal study), has a composition that was not precisely known. Both deficiencies have now been filled: the pattern can be unambiguously indexed on the monoclinic cell, and the composition is Cu_{1.938}S. The unit cell given for djurleite in Table 1 is slightly modified by this refinement with respect to that given by Potter and Evans (1976).

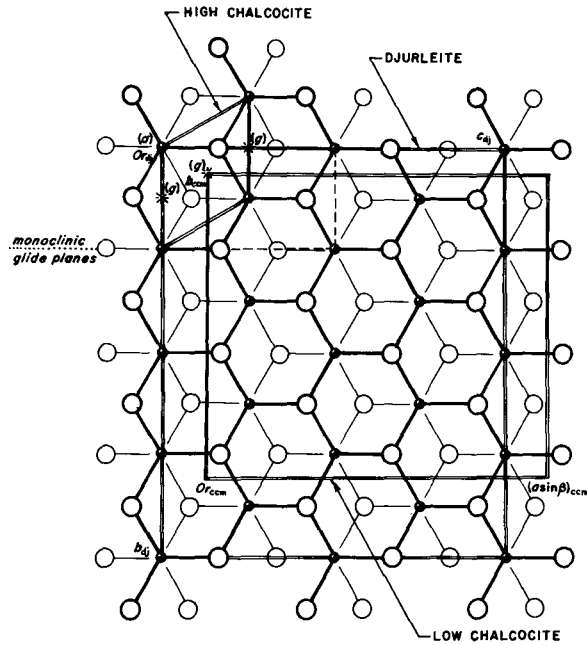


Fig. 2. View normal to the CuS layers in chalcocite and djurleite, showing relationships among the unit cells of high chalcocite, monoclinic low chalcocite (*ccm*) and djurleite (*dj*)

The direct cell transformations for vectors $\mathbf{X}(x, y, z)$ among the various lattices of hexagonal high chalcocite (*ch*), pseudo-orthorhombic low chalcocite (*cco*), monoclinic low chalcocite (*ccm*) and djurleite (*dj*) in the settings shown in Fig. 2 are given by the following matrices:

	← Left	→ Right
$\mathbf{X}_{ch} \leftrightarrow \mathbf{X}_{cco}$	$\begin{pmatrix} 3 & 4 & 0 \\ 0 & 8 & 0 \\ 0 & 0 & 2 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{3} & -\frac{1}{6} & 0 \\ 0 & \frac{1}{8} & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix}$
$\mathbf{X}_{cco} \leftrightarrow \mathbf{X}_{ccm}$	$\begin{pmatrix} 0 & 1 & 0 \\ \frac{1}{2} & 0 & 0 \\ -\frac{1}{2} & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 2 & 0 \\ -1 & 0 & 0 \\ 0 & 1 & 1 \end{pmatrix}$
$\mathbf{X}_{ch} \leftrightarrow \mathbf{X}_{ccm}$	$\begin{pmatrix} 2 & -3 & 0 \\ 4 & 0 & 0 \\ -1 & 0 & 2 \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{1}{4} & 0 \\ -\frac{1}{3} & \frac{1}{6} & 0 \\ 0 & \frac{1}{8} & \frac{1}{2} \end{pmatrix}$
$\mathbf{X}_{ch} \leftrightarrow \mathbf{X}_{dj}$	$\begin{pmatrix} 0 & 4 & 0 \\ 0 & 0 & 2 \\ 4 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \frac{1}{4} \\ \frac{1}{4} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \end{pmatrix}$

The reciprocal cell transformations for vectors \mathbf{H} (hkl) are obtained by transposing these matrices and exchanging left for right.

An important element in these structures consists of the layer of sulfur atoms in the hexagonal-close-packed framework, in which half of the triangle centers are occupied alternately by copper atoms. Figure 1 shows the unit cell of high chalcocite with these layers depicted. Actually at 125° C Wuensch and Buerger (1963) found that the copper sites are only 85% occupied, and Sadanaga, Ohmasa and Morimoto (1965) found even lower occupancies at other temperatures. Fully occupied layers with composition CuS are present in covellite, CuS (Evans and Konnert, 1976), and stromeyerite, AgCuS (Frueh, 1955). The centered orthohexagonal cell is shown by dashed lines in Figs. 1 and 2 to emphasize its relation to the supercells. In Fig. 2 a view normal to these layers is shown in which the rational supercell relationships to the hexagonal subcell defined in Table 1 are outlined. The centers of symmetry in the high chalcocite cell are at 2 (a), $(0, 0, 0; 0, 0, \frac{1}{2})$, and at 6 (g) $(\frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in the space group $P6_3/mmc$. In approaching the structure problem for low chalcocite and djurleite, we will try to place the origin of the supercell on one of these points.

Both the supercells have their unique b axes parallel to the hexagonal a axis of high chalcocite. The CuS layers are then normal to c in low chalcocite and normal to a in djurleite. An additional restriction on the relationship of the supercells to the subcell derives from the fact that the glide planes in the former must coincide with the mirror planes of the latter, and that the sulfur atoms must lie in or close to these glide planes. Thus, as Buerger and Buerger (1946) found by a more formal method, there can be no mirror plane normal to the glide plane and parallel to the pseudohexagonal c axis in low chalcocite, which means that if low chalcocite were orthorhombic it would have to be noncentrosymmetric. Now that we know that the supercells are monoclinic the last conclusion does not hold, and we may assume the space groups $P2_1/c$ or $P2_1/n$.

The restriction on the location of glide planes critically affects the possible (a) or (g) sites that are permissible for the origin of the supercells. Referring to the horizontal rows of sulfur atoms in Fig. 2 (normal to the hexagonal a axis direction), because the b axis of low chalcocite is 3 times the hexagonal a axis, and sulfur atoms must lie in the monoclinic glide planes at $y_{ccm} = \frac{1}{4}$ and $\frac{3}{4}$, the origin in low chalcocite can only lie halfway between the sulfur rows, that is, at the hexagonal (g) site at $\frac{1}{2}, \frac{1}{2}, 0$ (or $0, \frac{1}{2}, 0$). An ambiguity still remains, on the question as to whether the positive direction of the monoclinic a axis lies to the right or to the left in Fig. 2. For djurleite, where the monoclinic b axis is 4 times the hexagonal a axis, the origin must lie in the sulfur rows, and may be located at the site (a) $0, 0, 0$, or at the site (g) $\frac{1}{2}, 0, 0$. For each of these possible sites, the ambiguity with respect to the positive a axis direction also obtains.

As it happened, the structure of low chalcocite was solved directly by the symbolic addition procedure without regard to the above possible am-

biguities. In the case of djurleite, where the subcell reflections were considerably more dominant than in the case of low chalcocite, a strategy was required that examined each possible origin in turn. It should be observed that while we speak here of superstructures based on a simple substructure, the superstructure is not the displacive kind in which the larger structure is derived from small displacements of atoms from ideal or symmetrical positions in the substructure. Rather, the superstructure results from an ordering in particular sites of atoms which in the substructure are completely disordered over long distances. Thus, the special techniques for the solution of displacive type superstructures that have been developed in recent years cannot be applied in the case of chalcocite and djurleite. Also, because there are no fixed groups in these structures we cannot use any predetermined structural restraints in the solution or refinement of these structures. For example, although we may expect to find many CuS_3 triangular groups, the Cu–S and S–S distances may vary over a wide range, and cannot be constrained.

Structure analysis of low chalcocite

Many crystals were examined in a search for one suitable for structure analysis, but most either showed adverse twinning or proved to be mainly djurleite. The best material seemed to be that from the classical locality at Bristol, Connecticut. A large fragment was crushed in a steel mortar under liquid nitrogen to prevent any plastic deformation. Several of these anhedral crystals were examined by the precession method, always on the lookout (for no good reason) for monoclinic symmetry in the centered nets. Finally one was found that showed such lowered symmetry in a series of hkn patterns (mirror but no axial symmetry on upper levels), although strongly pseudo-orthorhombic, at least on the even lattice levels. The odd levels, which were considerably weaker than the even levels, showed clear monoclinic symmetry with no apparent pseudosymmetry. In fact, certain reflections such as $\bar{4}41$ (orthorhombic $\bar{4}71$) appeared moderately strong while the corresponding 341 reflection (orthorhombic $\bar{4}71$) was nearly absent. Thus it was concluded that the incipient twinning on (100) that is nearly universal in larger crystals was absent in this specimen. It was irregular but roughly pyramidal in shape, with a base 0.20×0.11 mm and height 0.08 mm. The base was bounded by (100), which is apparently a poorly developed cleavage plane.

Intensity data were collected with an automated Picker diffractometer, using Nb-filtered $\text{MoK}\alpha$ radiation. A total of 5155 independent reflections with $2\theta \leq 50^\circ$ were measured by $\theta/2\theta$ scan; 2931 of these registered intensities having $F > 3\sigma(F)$. These were corrected in the usual way for Lorentz and polarization effects, and then normalized to E values, at this stage without absorption corrections. The statistical distribution of the E values strongly indicated centrosymmetry, which was assumed in the solution of the structure. The largest value was 6.62 for 494 and the highest 14 reflections were substructure reflections. The highest nonsubstructure E value was 4.00 for 13.3.2. The origin was established by setting E 's positive for 494, 13.3.2, and 295 ($E = 3.00$). Phases were then developed by hand using the symbolic addition procedure for ~ 360 terms ($E > 1.50$). The process was smooth except for a group of reflections related to 1.8.10 ($E = 3.90$) for which an absolute phase could not be determined. Thus, a twofold ambiguity arose requiring two trial Fourier maps. Both E maps contained large numbers of prominent peaks in addition to those clearly associated with the hexagonal-close-packed sulfur framework, but for one these extra peaks were fairly uniform in height, arranged without unreasonably close contacts, and accounted well for the expected 24 copper atoms. The other map was far less well resolved, with many distorted and unreasonably closely spaced peaks. Thus, only the first choice was acceptable.

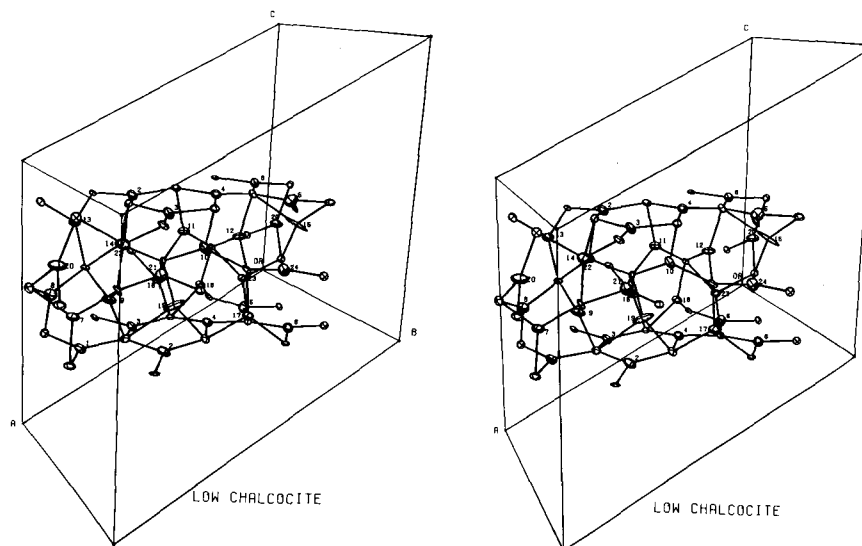


Fig. 3. Stereoscopic projection of a portion of the crystal structure of low chalcocite, showing the thermal ellipsoids at the 50% probability envelope. All copper atoms are numbered

An initial structure based on 24 Cu and 12 S atoms derived from the E map with overall $B = 1.0$ (109 parameters) gave a conventional reliability index $R = 0.42$ for 3288 data with $F > 2\sigma(F)$. In isotropic thermal mode (145 parameters) R was reduced to 0.163 after 9 cycles, and in anisotropic mode (324 parameters) to 0.118 after 6 more cycles. After several more trials, in which anomalous dispersion corrections were included and the data set reduced to 2897 with $F > 3\sigma(F)$ (with 34 strong reflections excluded for obvious extinction effects), but still with no absorption corrections and unit weights applied, R reached 0.108, and difficulties with nonpositive definite atoms were eliminated. At this point an ellipsoid drawing of the structure was prepared, which is shown in Fig. 3. The only unusual thermal anisotropies that appeared were those associated with Cu(15) and Cu(19). These were extremely elongated, suggesting some ambiguity about the coordination of these atoms, that is, something missing from the assumed model.

The suggestion is that Cu(15) and Cu(19) may each equally well lie in two possible sites, and this behavior may be accounted for either by letting each lie half time in each site, disordered in the same centrosymmetric space group; or a lower symmetry group (Pc or $P2_1$) may be assumed and the various sites occupied in an ordered way. A refinement was first attempted based on the split-atom model in $P2_1/c$, but this did not lead to any improvement in the reliability index. In this process, Cu(15) split into two half atoms separated by 0.62 Å with reasonable thermal motions, but the Cu(19) pair became only 0.2 Å apart and nonpositive definite. In the space group Pc , starting with the best model in $P2_1/c$ but with the atom pairs appropriately displaced, refinement was pursued with a reduction of R by about 0.2, but many atoms became nonpositive definite, many correlation coefficients ran over 0.95, and parameter errors became 3 or 4 times those obtained in the centrosymmetric refinement. After much effort was thus applied to refine a structure based on small displacements of atoms from the first centrosymmetric model in $P2_1/c$, all such attempts were abandoned as fruitless.

A closely similar situation was found recently by Lewis and Kupčik (1974) in the synthetic compound $\text{Bi}_2\text{Cu}_3\text{S}_4\text{Cl}$. One of the three kinds of copper atoms in the structure they determined

Table 2. Structure parameters for low chalcocite. $\sigma(x) = \sigma(y) = \sigma(z) = 0.0006$ for S, 0.0004 for Cu

Atom	<i>x</i>	<i>y</i>	<i>z</i>	\bar{u}_{rms} Å	Atom	<i>x</i>	<i>y</i>	<i>z</i>	\bar{u}_{rms} Å
S(1)	0.9575	0.0829	0.8422	0.13	Cu(7)	0.9345	0.1233	0.9923	0.17
S(2)	0.9413	0.0768	0.3462	0.12	Cu(8)	0.9414	0.1412	0.5099	0.17
S(3)	0.7940	0.0824	0.5068	0.10	Cu(9)	0.7615	0.2504	0.4109	0.17
S(4)	0.7917	0.0817	0.0060	0.12	Cu(10)	0.4429	0.1477	0.9348	0.16
S(5)	0.4491	0.0883	0.6133	0.12	Cu(11)	0.4254	0.1229	0.4388	0.15
S(6)	0.4444	0.0726	0.0957	0.12	Cu(12)	0.2578	0.2357	0.8507	0.17
S(7)	0.2999	0.0781	0.7868	0.12	Cu(13)	0.8209	0.0358	0.6830	0.15
S(8)	0.2843	0.0832	0.2869	0.11	Cu(14)	0.7830	0.0624	0.1671	0.18
S(9)	0.6960	0.2481	0.7220	0.13	Cu(15)	0.0261	0.2045	0.7722	0.26
S(10)	0.5479	0.2237	0.4167	0.11	Cu(16)	0.5026	0.0795	0.2834	0.16
S(11)	0.1970	0.2384	0.4766	0.12	Cu(17)	0.3022	0.0434	0.6230	0.19
S(12)	0.0483	0.2324	0.1332	0.12	Cu(18)	0.3050	0.0431	0.1339	0.16
Cu(1)	0.8645	0.2496	0.2927	0.15	Cu(19)	0.5243	0.2082	0.7543	0.24
Cu(2)	0.6171	0.0740	0.6765	0.16	Cu(20)	0.9992	0.0856	0.2166	0.18
Cu(3)	0.6102	0.0916	0.1677	0.15	Cu(21)	0.6227	0.1032	0.9531	0.16
Cu(4)	0.3628	0.2400	0.0731	0.14	Cu(22)	0.7037	0.1944	0.5659	0.17
Cu(5)	0.1276	0.0849	0.9451	0.18	Cu(23)	0.2028	0.2069	0.1398	0.17
Cu(6)	0.1065	0.0783	0.4429	0.15	Cu(24)	0.1308	0.0966	0.6791	0.17

(in space group $P2_12_12_1$) showed an extremely elongated ellipsoid. When they assumed this atom to be divided into two half-occupied positions, refinement placed them in two adjacent sites 0.63 Å apart, one in triangular coordination and one in linear coordination. The other two kinds of copper atoms were found to be in tetrahedral coordination.

Late in the refinement stages an absorption correction was applied by bounding the conchoidal fracture surfaces of the crystal by 8 planes. The linear absorption coefficient for $\text{MoK}\alpha$ was 238 cm^{-1} , and the transmission factors varied from 0.136 to 0.378. An isotropic extinction factor was also incorporated, with the strong reflections included. Final block refinement of the 36-atom model, with the data weighted according to $1/\sigma(F)$ as obtained from counting statistics, yielded $R = 0.086$ and R_w [based on $w\Delta(F^2)$] = 0.056. The resulting structure parameters are given in Table 2 and the thermal parameters are given in Table 3. A list of observed and calculated structure factors may be obtained on request from the author.

For all the calculations referred to above (and also those for djurleite), extensive use was made of the computer programs of the XRAY 76 system edited and written by James M. Stewart of the University of Maryland, and RFINE written by Larry W. Finger of the Geophysical Laboratory. Stereoscopic graphics were produced with ORTEP written by Carroll K. Johnson of the Oak Ridge National Laboratory. The computations were executed on IBM 370/155 and Honeywell 60/68 (with MULTICS) systems. Atomic scattering factors for neutral Cu and S as represented analytically by Doyle and Turner (1968) were used throughout. The anomalous dispersion factors and mass absorption coefficients of Cromer and Liberman (1970) were used in the treatment of the data.

Structure analysis of djurleite

As in the case of low chalcocite, the structure of djurleite could not be studied until truly single, untwinned crystals could be obtained. Such crystals became available recently from a specimen

