

The Crystal Structure of Synthetic Mooihoekite, $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ *

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Mooihoekite, $\text{Cu}_9\text{Fe}_9\text{S}_{16}$, is a recently characterized mineral that is closely related to chalcopyrite, CuFeS_2 , talnakhite, $\text{Cu}_{10}\text{Fe}_8\text{S}_{16}$, and haycockite, $\text{Cu}_4\text{Fe}_5\text{S}_8$. A synthetic mooihoekite crystal was used in a three-dimensional X-ray structure analysis. The crystal cell is tetragonal, $P\bar{4}2m$, with $a = 10.585$ (5), $c = 5.383$ (5) Å, $Z = 1$ and $D_x = 4.37$. The super-lattice nature of the structure required that special attention be given to low-intensity reflexions. Three sets of intensity data were collected on a 4-circle diffractometer. The presence of twinning [twin plane {201}] required that separate data be collected for the four additional twin-components. Absorption corrections were applied. The structure is a sphalerite-like arrangement of metal and sulphur atoms with two additional metals at interstitial sites. Information on the order and disorder of the metals was obtained both from the X-ray analysis and from previously reported magnetic and Mössbauer data. The structural parameters were refined by full-matrix least-squares methods to R values of 0.205 (all data) and 0.047 ('less thans' omitted).

Introduction

Mooihoekite, $\text{Cu}_9\text{Fe}_9\text{S}_{16}$, is a recently characterized mineral that is compositionally and structurally similar to chalcopyrite, CuFeS_2 , talnakhite, $\text{Cu}_{10}\text{Fe}_8\text{S}_{16}$, and haycockite, $\text{Cu}_4\text{Fe}_5\text{S}_8$. Mooihoekite and haycockite were shown to be distinct minerals after a detailed chemical, optical, magnetic, and X-ray diffraction study of sulphide-bearing ore from the Mooihoek Farm area, Transvaal, South Africa (Cabri & Hall, 1972). These studies were undertaken in association with a detailed investigation of the central portion of the Cu-Fe-S system (Cabri, 1973).

Mooihoekite has been synthesized in this laboratory and is similar to the high-temperature ' γ -phase', reported by Hiller & Probsthain (1956), except that it is stable at room temperature. In most respects, the synthetic material is superior in homogeneity and crystallinity to the natural mineral and, for these reasons, it was used in the previously reported magnetic and Mössbauer measurements (Townsend, Horwood, Hall & Cabri, 1971), and in this study. Townsend *et al.* (1971) reported that the magnetic susceptibilities of mooihoekite had a large temperature-independent component (9×10^{-6} e.m.u. g^{-1}), as well as a temperature-dependent component, consistent with a partly disordered antiferromagnetic structure. The Mössbauer spectrum is consistent with metals occupying some of the sites that are vacant in a chalcopyrite-like arrangement of atoms.

This X-ray investigation was undertaken to provide accurate information on the atomic coordinates and thermal parameters, and to identify the metal ordering in the structure where feasible. To this latter end, the recently refined structural parameters of chalcopyrite (Hall & Stewart, 1973) and cubanite, CuFe_2S_3 , (Szymanski, 1973) were utilized.

Experimental

Crystal data

Source: synthetic sample no. 179 (Cabri, 1973).
Microprobe analysis of no. 179 in at. % (Cabri & Hall, 1972): Cu: 26.41 (10), Fe: 26.44 (14), S: 47.16 (2).
Chemical composition: $\text{Cu}_{1.120}\text{Fe}_{1.121}\text{S}_{2.00}$.
Stoichiometric formula: $\text{Cu}_9\text{Fe}_9\text{S}_{16}$.
Systematic hkl absences: none.
Space group: $P\bar{4}2m$ (No. 111).
Cell dimensions: $a = 10.585$ (5), $c = 5.383$ (5) Å;
 $Z = 1$, $D_{\text{meas}} = 4.36$ g cm^{-3} , $D_{\text{calc}} = 4.37$ g cm^{-3} .

Linear absorption coefficient: $\mu(\text{Mo } K\alpha) = 146.9$ cm^{-1} .
Intensity data: 1614 reflexions measured (three times).

Several small crystals of synthetic mooihoekite were obtained from Dr L. J. Cabri of the Mineral Sciences Division. Gandolfi-camera X-ray powder patterns showed these crystals to be essentially identical with those of natural mooihoekite but with significantly sharper line profiles. Single-crystal X-ray precession photographs showed all crystals to be twinned about the {201} twin planes. Natural mooihoekite fragments also exhibit this twinning in addition to considerable microcrystallinity and high mosaicity. A synthetic crystal which had a single dominant twin-component was selected for this analysis. It was irregular square-pyramidal in shape with widths between 0.06 and 0.09 mm. Because of the small size and relative scarcity of suitable single crystals, no attempt was made to grind a sphere.

Initial examination of the precession films showed only reflexions satisfying the hkl condition $h+k=2n$, and the tetragonal Laue group $4/mmm$. However, subsequent detailed study of the films, along with additional evidence obtained during data collection, revealed several reflexions that violated this condition. The possible space groups were, therefore, $P4/mmm$, $P\bar{4}2m$, $P4m2$, $P4mm$, and $P422$. The super-lattice hkl

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pattern of the intense reflexions that is present in the data, with $h, k = 2n$, is characteristic of chalcopyrite-like structures and denotes the presence of a sphalerite-like cubic subcell ($a \approx 5.3 \text{ \AA}$). The tetrahedral coordination of such a subcell necessitates the choice of the space group $P\bar{4}2m$ (No. 111).

The crystal was mounted on a Picker 4-circle diffractometer and the orientation of the major twin-component was located consistent with the precession film data. Alignment of suitable reflexions permitted the determination of the orientation matrix and final cell parameters for the major twin-component. Considerable care was required in selecting these reflexions because those significantly affected by the minor twin-components could not be used. The angles 2θ , χ and ω were obtained from an automatic alignment process (Busing, 1970) on eight equivalent 884 reflexions, four equivalent 12,12,0 reflexions and eight equivalent 12,0,6 reflexions assuming a triclinic cell. The refined unit-cell values were $a = b = 10.585 (5) \text{ \AA}$, $c = 5.383 (5) \text{ \AA}$ and $\alpha = \beta = \gamma = 90.00 (1)^\circ$. Orientation matrices were similarly determined for the minor components, but with less accuracy.

The minor twin-components result from the four $\{201\}$ planes of the major component acting as twin planes (see Fig. 1). The refined orientation matrices give $\angle [h00]/[00l]_T = 0.98^\circ$ for each of the minor components and this compares favourably with a value of 0.97° calculated from the cell dimensions. The overall result of the twinning on the diffraction data is that some reflexions with $h = 2n$ or $k = 2n$ have contributions from more than one component. The relative proportions of twin components were determined from intensity measurements of the 330 and 040 reflexions. The ratio of the five twin components were 1.000:0.109 (4):0.035 (7):0.013 (1):0.008 (2).

The intensity data for mooihoekite were collected on an automatic 4-circle diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation. The $\theta/2\theta$ scan width (2.5 to 3.2°) was adjusted for dispersion, and the background counts were measured on each side of the peak for approximately the same length of time as that taken for the scan. The intensities of two reference reflexions were recorded after every 50 measurements in order to monitor the crystal alignment and instrument stability. No significant variations were noted during the data collection.

An asymmetric set of reflexions was collected three times for the major twin-component in order to provide greater reliability in the measurement of the low intensities which represented a large proportion of the data. The intensities of equivalent reflexions were averaged into a unique set in preparation for the adjustment of twin overlap. For the four minor twin-components only data where reflexions overlapped those of the major component were collected.

Many intensities in the minor twin-component data were greater than the known twin proportions would permit; these resulted from the overlap of major com-

ponent intensities. The identification of reflexions affected by overlap was used in the reverse sense to compensate for twinning contributions in the merged intensity data. The adjustments also required a knowledge of the relative orientation of the minor components because the twinning coincided only for certain φ and χ values and at low 2θ angles.

Following adjustments to the intensities for twinning, the merged set of hkl data was corrected for absorption effects with a generalized Gaussian procedure (Gabe & O'Byrne, 1970). For the purposes of structure refinement the intensity data were considered in two different ways. First, reflexions with net measured intensities below the 10% significance level were set to a value of $1.65\sigma (I)$ and coded, for refinement purposes, as 'less than'. With this criterion, all but 409 of the 1614 reflexions were considered as 'less thans'. In a second data set, all reflexions were included at their measured net intensities except those values which calculated negative, which were set equal to zero. The initial structure solution and refinement were performed with the intensity data treated in the first way (*i.e.* with 'less thans'), but the final least-squares refinement used intensities at their measured values.

Structural determination

The super-lattice pattern of intense reflexions with $h, k = 2n$ indicated that the dominant structural feature in mooihoekite, as in other chalcopyrite-like minerals, is the sphalerite-like tetrahedral arrangement of the sulphur and metal atoms. On this basis, the first structure factors were calculated with 16 sulphur atoms at the $P\bar{4}2m$ sites $8o$ ($0.125, 0.625, 0.250$), $4n$ ($0.125, 0.125, 0.250$) and $4n$ ($0.375, 0.375, 0.250$); and 16 copper-iron atoms at sites $4n$ ($0.25, 0.25, 0.50$), $4l$ ($0.25, \frac{1}{2}, 0$), $4i$ ($0.25, 0, 0$), $2f$ ($\frac{1}{2}, 0, \frac{1}{2}$), $1c$ ($0, 0, \frac{1}{2}$), and $1b$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). This, and all subsequent calculations, were performed on the CDC 6400 computer with the X-RAY system of crys-

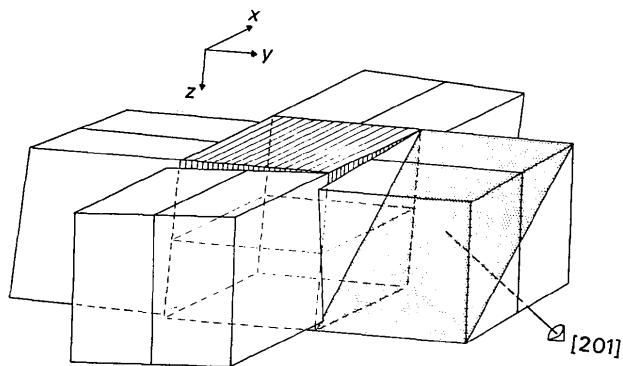


Fig. 1. A real-space representation of the twinning components in mooihoekite. The major twin-component in the form of a double cell (cross-hatched) is surrounded by the four minor twin-components in their orientations. A (201) twin plane is shown stippled for one double cell. The axial system refers to the major twin-component.

Table 1. Thermal parameters and coordination of atoms in some Cu-Fe-S minerals

| Chalcopyrite (Hall & Stewart, 1973) | | Cubanite (Szymanski, 1973) | | Coordination: T. tetrahedral TBP. trigonal bipyramidal O. octahedral | | Qualifier: R. regular IR. irregular D. distorted | | Mooihoekite (This work) | | |
|--|--------------|-------------------------------|--------------|---|--------------|---|-------------------|------------------------------|--------------|-------------------|
| <i>I</i> 42 <i>d</i> site | Atom type | <i>Pcmm</i> site | Atom type | <i>I</i> 43 <i>m</i> site | Atom type | Talnakhite (Hall & Gabe, 1972)* | Coordi- nation | <i>P</i> 42 <i>m</i> site | Atom type | Coordi- nation |
| Cu(4a) | Cu | Cu(4c) | Cu | M1(2a) | Fe | Fe | R.T.† | M1(4n) | Cu | IR.T. |
| Fe(4b) | Fe | Fe(8d) | Fe | M2(12e) | Cu† | Cu† | IR.T.† | M2(4l) | Fe | IR.T.† |
| | | | | M3(12d) | Fe | Fe | R.T. | M3(4i) | Cu | IR.T.† |
| | | | | M4(8c) | Cu | Cu | IR.T. | M4(2f) | Fe | R.T. |
| | | | | | | | | M5(1c) | Fe | R.T.† |
| | | | | | | | | M6(1b) | Cu | IR.T.† |
| | | | | | | | | M7(1a) | Fe | IR.T.† |
| | | | | | | | | M8(1d) | Fe | IR.T.† |
| S(8d) | S | S1(4c) | S | S1(8c) | S | S | D.TBP. | S1(8o) | S | IR.T. |
| | | S2(8d) | S | S2(24g) | S | S | IR.T. | S2(4n) | S | D.TBP. |
| | | | | | | | | S3(4n) | S | D.TBP. |

* A recent refinement involving metal-types.

† Metal ratio Cu:Fe=0.83:0.17.

‡ Additional close metal-to-metal distance(s) of about 2.7 (2) Å.

tallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). An isotropic temperature factor of 1.0 Å² was used along with the neutral atomic scattering factors of Cromer & Waber (1965). The scattering factor for the copper-iron atoms was approximated as the average $0.5[f(\text{Cu})+f(\text{Fe})]$. The structure-factor calculation had an R value ($\sum|\Delta F|/\sum|F_o|$) of 0.35 ('less thans' omitted).

A subsequent electron-density difference map showed large positive maxima at the sites 1a (0,0,0), 1d ($\frac{1}{2}, \frac{1}{2}, 0$) and 2e ($\frac{1}{2}, 0, 0$). This indicated that the two metal atoms as yet unaccounted for in this structure should be located at these interstitial sites. However, if these sites are fully occupied, and this was expected from the cell proportions, the two atoms can be located only at sites 1a and 1d or at 2e. Because these sites are equivalent in the ideal sphalerite-like model, an arbitrary choice of one set can be made for the purpose of initial refinement. Sites 1a and 1d were selected because of the flexibility of this model in the allocation of metal types.

A difference map, from structure factors calculated with two additional (Cu, Fe) atoms, showed substantial shifts of both metal and sulphur atoms away from these new sites. Successive cycles of full-matrix least-squares refinement were used with the first data set to refine both the coordinates of the isotropic temperature factors of the S and (Cu, Fe) atoms to an R value of 0.085 ('less thans' omitted). Unit weights were used throughout the least-squares refinement. It was evident that further refinement of the model would require an identification of the metal-ordering in the structure. Up to this point, it had been assumed that coordinate shifts from the ideal sphalerite-like structure resulted largely from steric hindrance with the extra metals. Although this subsequently proved to be a valid assumption, it was also possible that the coordinates of the sulphur atoms were significantly affected by the metal types to which they were bonded. It has been demonstrated, in the refinements of chalcopyrite (Hall & Stewart, 1973) and talnakhite,* that the identification of metal types is necessary before reliable refinement of the sulphur parameters can proceed.

The similarity in electron-density distribution of copper and iron atoms poses a problem in X-ray diffraction analyses. In the simpler well-ordered Cu-Fe sulphide structures such as chalcopyrite, CuFeS₂, and cubanite, CuFe₂S₃, it is possible with good intensity data to distinguish unambiguously the metal types on electron-density grounds alone. In more complex structures such as mooihoekite it is a much more difficult task to identify the metal types, and whether, in fact, a given site is disordered. For this reason, considerable care was taken in the data collection process to ensure that the weak to medium intensities were measured as precisely as possible because these are the reflexions

* A recent refinement of the talnakhite data reported by Hall & Gabe (1972), using assigned metal types.

that are most sensitive to distortions from the basic sphalerite-like sub-cell and to the metal ordering.

The recent refinements of chalcopyrite (Hall & Stewart, 1973) and cubanite (Szymanski, 1973) indicate that the Cu and Fe atoms in the chalcopyrite-like structures can be distinguished by isotropic thermal motion and atomic coordination in addition to electron-density differences. The summary of these data, for chalcopyrite, cubanite, and talnakhite (see Table 1), shows that the isotropic temperature factors are, in general, lower for iron atoms than for copper atoms. In the more complex Cu-Fe-S structures, this could be due to the mis-identification of a metal as a copper or an iron atom, rather than as a disordered (Cu, Fe) atom. However, the consistency of values for the well ordered structures of chalcopyrite and cubanite supports the concept that the thermal motion is a function of the bonding associated with each atom-type. These values should, therefore, reflect the ionic-covalent interaction between atoms, and/or the magnetic coupling interaction of the iron atoms.

In chalcopyrite, the tetrahedral coordination of the iron atom is perfectly regular, but that of the copper atom is not. These differences in coordination with atom type also occur in the structure of talnakhite (Hall & Gabe, 1972) and were used to assist in the identification of copper and iron atom sites in mooihoeite. In sites *1c*, *1b*, *1a*, and *1d*, the metals could not be identified directly, so different metal combinations were tested as structural models in the refinement process. Successive cycles of full-matrix least-squares refinement were used with the first set of data to refine the atomic positional and isotropic thermal parameters in each model. The best model ($R=0.065$, 'less than' omitted) was shown to be that with Cu atoms at sites *4n*, *4i* and *1d*, and Fe atoms at sites *4l*, *2f*, *1c*, *1b* and *1a*.

Before refinement could continue it was necessary to correct for anomalous dispersion. The space group $P\bar{4}2m$ permits two enantiomorphic structures that can both be defined in terms of right-handed cell axes. It was necessary, therefore, to identify which of these had been implicitly defined at the time of data collection by the arbitrary choice of cell axes. The anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ for Cu, Fe, and S (Cro-

mer & Libermann, 1970) were included in the least-squares refinement process of the two enantiomorphic structures x, y, z and x, y, \bar{z} . Convergence to R values of 0.069 and 0.058 respectively indicated that the latter configuration was consistent with the initial choice of axes and was used in further refinement.

In addition, although the mooihoeite crystal exhibited a relatively high mosaicity during the data collection process, at least four of the most intense reflexions were attenuated significantly by extinction effects and were omitted in subsequent least-squares calculations. It was also necessary at this stage to consider the effect of the probable ionic state of the atoms on the scattering factors used in the refinement process. As with the structure of chalcopyrite (Hall & Stewart, 1973), the effective ionic configuration of atoms in mooihoeite is expected to be somewhere in the range of $\text{Cu}^+\text{Fe}^{3+}\text{S}_2^{2-}$ to $\text{Cu}^{2+}\text{Fe}^{2+}\text{S}_2^{2-}$.

The Cu^+ and Fe^{3+} curves of Cromer & Waber (1965), and the S^{2-} curve of Tomiie & Stam (1958), were selected as suitable approximations for further calculations. Three cycles of isotropic least-squares refinement reduced the R value to 0.050 and improved the overall agreement, particularly in the low-angle region of the data.

At this point, the relative instability of the isotropic thermal parameters associated with atoms Fe(*1c*), Fe(*1b*), Fe(*1a*), and Cu(*1d*) became a limiting factor to the least-squares process. A review of the metal-ordering based both on the thermal and stereochemical information discussed above and on the difference synthesis, indicated that the metals at sites *1b* and *1d* should be changed to Cu and Fe atoms, respectively. In addition, there were high correlation coefficients (12 exceeded 0.9) between parameters associated with these and other atoms due, in large part, to an unfavourable ratio of intensities considered significant at the 10% level to parameters for specific sites. It was necessary, therefore, to continue the refinement with the second data set where all reflexions were considered at their net measured intensities. When this was done no correlation coefficient exceeded 0.46 and the previously unstable thermal parameters converged to values reasonably consistent with the allocation of atom type. An-

Table 2. *Final atomic parameters and standard deviations (in parentheses)*

The anisotropic temperature factors are expressed in the form $T = \exp[-2\pi(U_{11}a^{*2}h^2 + 2U_{12}a^*b^*hk + \dots)]$.

The isotropic temperature factors $\langle B \rangle$ (in \AA^2) were calculated from the U_{ij} values.

| Atom Type | Site | x/a | y/b | z/c | $U_{11} \times 10^2$ | $U_{22} \times 10^2$ | $U_{33} \times 10^2$ | $U_{12} \times 10^2$ | $U_{13} \times 10^2$ | $U_{23} \times 10^2$ | $\langle B \rangle$ | |
|-----------|------|-----------|---------------|---------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|---------------------|------|
| M1 | Cu | <i>4n</i> | 0.2507 (2) | 0.2507 (2) | 0.4881 (8) | 2.1 (1) | 2.1 (1) | 1.9 (1) | 0.2 (1) | 0.2 (1) | 0.2 (1) | 1.60 |
| M2 | Fe | <i>4l</i> | 0.2423 (3) | $\frac{1}{2}$ | 0 | 1.3 (1) | 1.3 (1) | 1.2 (1) | 0 | 0 | 0.6 (1) | 1.02 |
| M3 | Cu | <i>4i</i> | 0.2583 (2) | 0 | 0 | 1.3 (1) | 1.8 (1) | 1.9 (1) | 0 | 0 | 0.3 (2) | 1.31 |
| M4 | Fe | <i>2f</i> | $\frac{1}{2}$ | 0 | $\frac{1}{2}$ | 1.3 (1) | 1.0 (1) | 1.1 (1) | 0 | 0 | 0 | 0.90 |
| M5 | Fe | <i>1c</i> | 0 | 0 | $\frac{1}{2}$ | 1.5 (1) | 1.5 (1) | 1.1 (2) | 0 | 0 | 0 | 1.05 |
| M6 | Cu | <i>1b</i> | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 1.9 (1) | 1.9 (1) | 1.5 (2) | 0 | 0 | 0 | 1.40 |
| M7 | Fe | <i>1a</i> | 0 | 0 | 0 | 0.3 (1) | 0.3 (1) | 0.8 (2) | 0 | 0 | 0 | 0.37 |
| M8 | Fe | <i>1d</i> | $\frac{1}{2}$ | $\frac{1}{2}$ | 0 | 1.7 (1) | 1.7 (1) | 1.1 (2) | 0 | 0 | 0 | 1.20 |
| S1 | S | <i>8o</i> | 0.1236 (3) | 0.3772 (3) | 0.2566 (8) | 1.0 (1) | 1.6 (1) | 1.2 (1) | -0.2 (1) | -0.0 (1) | -0.2 (1) | 1.02 |
| S2 | S | <i>4n</i> | 0.1237 (3) | 0.1237 (3) | 0.7497 (9) | 1.1 (1) | 1.1 (1) | 1.1 (2) | 0.1 (1) | -0.1 (1) | -0.1 (1) | 0.87 |
| S3 | S | <i>4n</i> | 0.3733 (3) | 0.3733 (3) | 0.7645 (9) | 1.2 (1) | 1.2 (1) | 1.4 (2) | -0.2 (1) | 0.0 (1) | 0.0 (1) | 1.01 |

isotropic temperature factors were introduced for all atoms and the data set converged in four cycles to reliability indices comparable with the precision of the measured intensities. The final R value for all data was 0.205. The magnitude of this value arises from the large proportion of weak intensities present in the data and suggests that this quantity is of questionable use in assessing the reliability for structures of this nature. This is further emphasized by the fact that when the 'less thans' are omitted from the least-squares refinement the final

R value is 0.046 but the standard deviations for all parameters are larger and the thermal parameters for the atoms at sites 1c, 1b, 1a and 1d are almost indeterminate.

As noted above, the initial electron-density difference map showed large positive maxima at the site 2e (1/2, 0, 0) as well as at 1a (0, 0, 0) and 1d (1/2, 1/2, 0), and the two additional metal atoms were located at sites 1a and 1d to permit flexibility of the allocation of metal types. Although the refinement of the model, described above,

Table 3. Structure factors listed in blocks of constant hk in columns of I, [Fm] x 10 and [Fc] x 10. E denotes reflexions affected by secondary extinction and omitted from the final refinement.

Table with multiple columns of numerical data representing structure factors for various reflections (hk).

resulted in both these sites being occupied by Fe atoms, this does not imply, of necessity, that the correct site is $2e$ because the environments of sites $1a$ and $1d$ are not identical. In order to test whether an alternate structure with metal atoms occupying site $2e$ is possible, least-squares refinement on this structure was performed. The higher R value of 0.065 ('less than' omitted) suggests that the placing of the additional metal atoms at the sites $1a$ and $1d$ is correct.

The final atomic parameters, refined with the intensities as measured, are listed in Table 2, and the measured and calculated structure factors are listed in Table 3.

Description of the structure

This study has shown that the structure of mooihoekite (Fig. 2) is based on a sphalerite-like arrangement of metal and sulphur atoms. Previous determinations of the structures of chalcopyrite (Pauling & Brockway, 1932) and of talnakhite (Hall & Gabe, 1972), and a preliminary X-ray analysis of haycockite, indicate that these structures are also based on the sphalerite-like subcell. In contrast, cubanite, CuFe_2S_3 , another Cu-Fe-S mineral associated with chalcopyrite in some mineral deposits, has an orthorhombic structure that is essentially 'wurtzitic' in nature. It has recently been shown (Cabri, Hall, Szymanski & Stewart, 1973), however, that this structure transforms directly to a cubic phase ($a \approx 5.3 \text{ \AA}$) on moderate heating, with a sphalerite-like disordered structure. The structures of all minerals with compositions in the central portion of the Cu-Fe-S system, therefore, exist at some temperature as a sphalerite-like ABC arrangement of close-packed layers of sulphur atoms that are tetrahedrally coordinated to the copper and iron atoms.

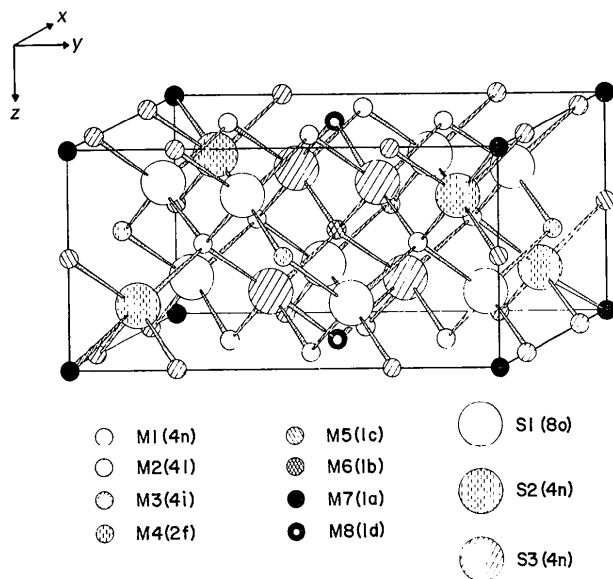


Fig. 2. Unit-cell model showing the crystal structure of mooihoekite in terms of the independent atomic sites for space group $P\bar{4}2m$.

It should be stressed, prior to reviewing the structural parameters of mooihoekite, that the metal-types allocated to specific atomic sites as listed in Table 2 and

Table 4. *Interatomic distances and angles (calculated from coordinates in Table 1)*

Standard deviations are in parentheses.

Atoms not at x, y, z are specified as follows:

| | | | | | | | |
|-----|-------|-------|-------|-----|-------|-------|-------|
| a | x | y | $1+z$ | b | $1-y$ | x | $-z$ |
| c | $-y$ | x | $-z$ | d | $-y$ | x | $1-z$ |
| e | $-x$ | $1-y$ | z | f | x | $1-y$ | $1-z$ |
| g | $-x$ | y | $1-z$ | h | x | $1-y$ | $-z$ |
| i | y | x | z | j | $-x$ | y | $-z$ |
| k | x | y | $z-1$ | l | $-x$ | $-y$ | z |
| m | $-x$ | y | $2-z$ | n | $1-x$ | y | $2-z$ |
| o | $1-x$ | $1-y$ | z | p | $1-x$ | y | $1-z$ |
| q | y | $-x$ | $-z$ | r | x | $-y$ | $1-z$ |
| s | $1-y$ | x | $1-z$ | t | y | $-x$ | $1-z$ |
| u | $1-y$ | $-x$ | z | | | | |

Distances (\AA)

| | | | |
|--------|----------|--------|----------|
| M1-M2 | 3.73 (2) | S2-M7a | 2.29 (2) |
| M1-M2a | 3.82 (2) | S3-M1 | 2.36 (2) |
| M1-M3 | 3.73 (2) | S3-M2a | 2.31 (2) |
| M1-M3a | 3.83 (2) | S3-M6 | 2.37 (2) |
| M1-M4 | 3.74 (2) | S3-M8a | 2.28 (2) |
| M1-M5 | 3.75 (2) | S1-S1e | 3.69 (2) |
| M1-M6 | 3.73 (2) | S1-S1f | 3.69 (2) |
| M2-M2b | 3.86 (2) | S1-S1g | 3.70 (2) |
| M2-M3c | 3.62 (2) | S1-S1h | 3.79 (2) |
| M2-M4d | 3.72 (2) | S1-S1i | 3.80 (2) |
| M2-M6 | 3.83 (2) | S1-S1j | 3.81 (2) |
| M2-M8 | 2.73 (1) | S1-S2g | 3.75 (2) |
| M3-M3c | 3.87 (2) | S1-S2 | 3.77 (2) |
| M3-M4 | 3.71 (2) | S1-S2k | 3.83 (2) |
| M3-M5 | 3.84 (2) | S1-S3k | 3.74 (2) |
| M3-M7 | 2.73 (1) | S1-S3f | 3.74 (2) |
| M5-M7 | 2.69 (1) | S1-S3 | 3.80 (2) |
| M6-M8 | 2.69 (1) | S2-S2l | 3.70 (2) |
| S1-M1 | 2.27 (2) | S2-S2g | 3.75 (2) |
| S1-M2 | 2.28 (2) | S2-S2m | 3.76 (2) |
| S1-M3c | 2.28 (2) | S2-S3 | 3.74 (2) |
| S1-M4d | 2.26 (2) | S3-S3n | 3.69 (2) |
| S2-M1 | 2.37 (2) | S3-S3o | 3.79 (2) |
| S2-M3a | 2.36 (2) | S3-S3p | 3.91 (2) |
| S2-M5 | 2.29 (2) | | |

Angles ($^\circ$)

| | | | |
|------------|-----------|------------|-----------|
| S1-M1-S1i | 113.4 (3) | M1-S1-M2 | 110.1 (2) |
| S1-M1-S2 | 109.0 (2) | M1-S1-M3c | 110.3 (2) |
| S1-M1-S3 | 110.3 (2) | M1-S1-M4d | 111.3 (2) |
| S2-M1-S3 | 104.4 (3) | M2-S1-M3c | 105.3 (2) |
| S1-M2-S1h | 113.0 (2) | M2-S1-M4d | 110.0 (2) |
| S1-M2-S3k | 109.5 (1) | M3c-S1-M4d | 109.6 (2) |
| S1-M2-S3f | 109.3 (2) | M1-S2-M3a | 108.2 (2) |
| S3f-M2-S3k | 106.2 (2) | M1-S2-M5 | 107.5 (2) |
| S1i-M3-S1q | 113.0 (2) | M3a-S2-M3d | 110.2 (2) |
| S1q-M3-S2k | 107.8 (2) | M3a-S2-M5 | 111.3 (2) |
| S1i-M3-S2k | 111.2 (1) | M1-S2-M7a | 179.5 (3) |
| S2k-M3-S2r | 105.6 (2) | M3a-S2-M7a | 72.1 (2) |
| S1s-M4-S1t | 109.2 (2) | M5-S2-M7a | 72.0 (1) |
| S1i-M4-S1s | 109.3 (2) | M1-S3-M2a | 109.6 (2) |
| S1s-M4-S1u | 109.8 (2) | M1-S3-M6 | 104.1 (2) |
| S2-M5-S2l | 108.0 (2) | M2a-S3-M2s | 113.4 (2) |
| S2-M5-S2g | 110.2 (2) | M2a-S3-M6 | 109.9 (2) |
| S3-M6-S3o | 106.2 (2) | M1-S3-M8a | 174.7 (2) |
| S3-M6-S3f | 111.1 (2) | M2a-S3-M8a | 72.9 (2) |
| S2g-M7-S2r | 107.9 (2) | M6-S3-M8a | 70.6 (1) |
| S2k-M7-S2r | 110.3 (2) | | |
| S3f-M8-S3p | 112.5 (2) | | |
| S3k-M8-S3p | 108.0 (2) | | |

displayed in Fig. 3, are not unequivocal. This is particularly the case for the metals at sites 1c, 1b, 1a, and 1d, because the parameters pertaining to these sites are largely dependent on the classes of reflexions with very weak intensities.

The atomic coordinates listed in Table 2 and the interatomic distances listed in Table 4 show a substantial shift ($\sim 0.10 \text{ \AA}$) of the Cu(4i) atoms from the 'ideal' position in the sphalerite-like subcell ($a/2 \approx 2.64 \text{ \AA}$). This shift is in a direction consistent with the presence

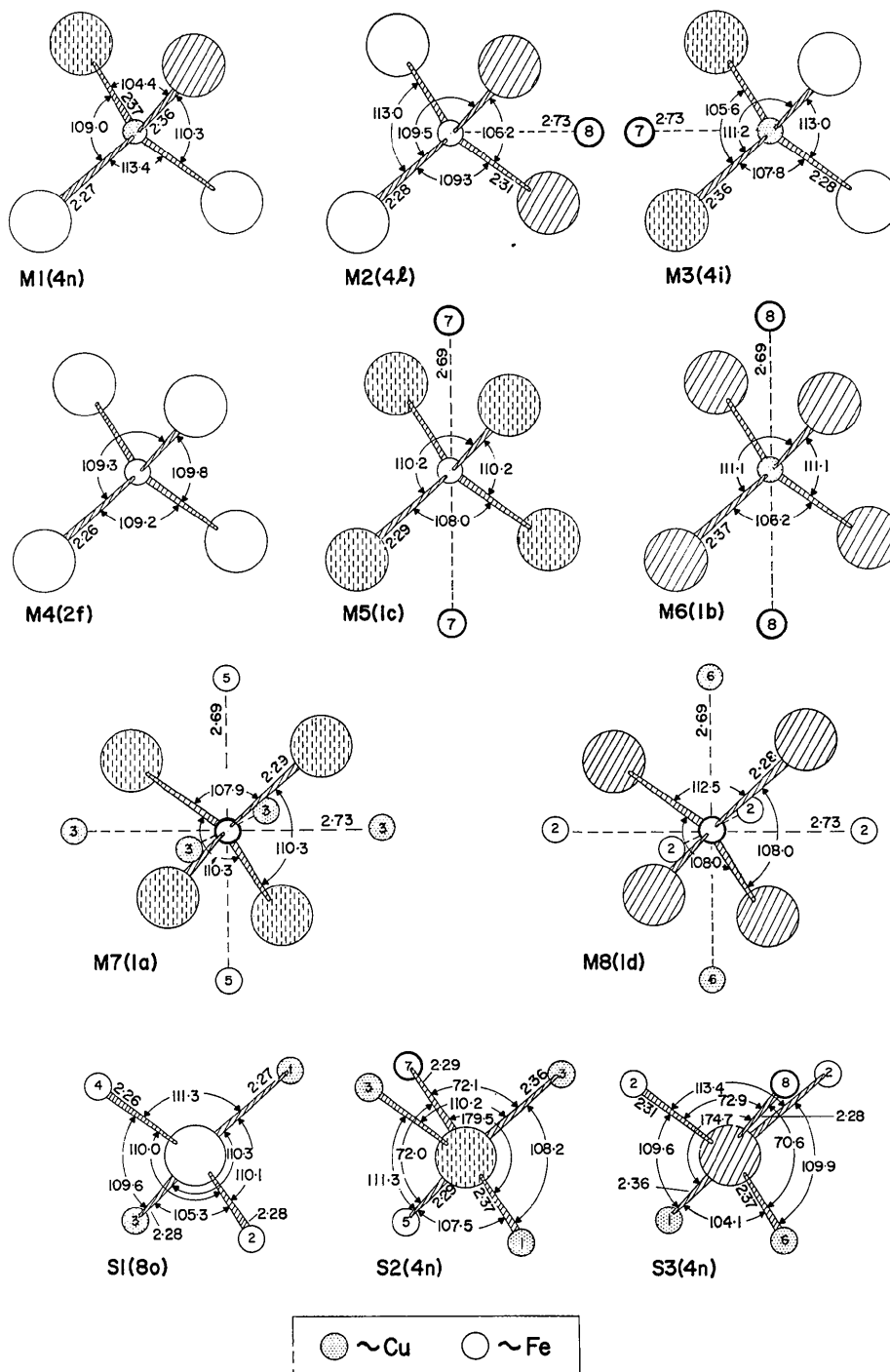


Fig. 3. The coordination of each independent atom in mooihoekite with the interatomic distances (Å) and angles (°).

of the interstitial Fe atom at site *1a*. The displacement of the Fe(*1c*) atom (0.05 Å) which results in an expansion of the *c* cell parameter agrees with the close proximity of Fe(*1a*). The relative magnitude of these displacements is consistent with the higher degree of steric freedom at the Cu(*4i*) site and the necessity for the displacement of Fe(*1c*) to distort the entire crystal lattice. Similar explanations may be given for the 0.09 Å shift of Fe(*4l*) and the 0.05 Å displacement of Cu(*1b*) from the interstitial atom Fe(*1d*).

Shifts of the sulphur atom from the ideal sites in the sphalerite-like *fcc* matrix are best discussed in terms of the metal coordination. The coordinations about the individual atoms are displayed in Fig. 3, with the bond lengths and angles. The average interatomic distances $\langle\text{Cu-S}\rangle = 2.33$ and $\langle\text{Fe-S}\rangle = 2.28$ Å are consistent with expansion of corresponding distances 2.302 and 2.257 Å in chalcopyrite (Hall & Stewart, 1973), due to the interstitial atoms. There is a wide range of metal-sulphur distances on either side of the average values, and this is another indication of steric hindrance due to interstitial atoms on the ionic-covalent bonding. Because of this, an analysis of individual bond lengths is not likely to provide reliable information about the nature of bonding. A possible exception is about the Fe(*2f*) site because this is the only metal-coordinated tetrahedron. Here the Fe-S distance of 2.26 (2) Å agrees with that determined in chalcopyrite, 2.257 (1) Å.

The interatomic angles are also largely dependent on the proximity of the interstitial atoms. Metal-coordinated tetrahedra which share an edge [*viz.* Fe(*4l*) and Cu(*4i*)] subtend smaller angles of 106.2 and 105.6° with that edge, in agreement with this type of coordination in talnakhite (105.8°) and cubanite (104.8°). In chalcopyrite, the Fe-tetrahedra are perfectly regular, but the Cu-tetrahedra are flattened (Hall & Stewart, 1973). In mooihokite only two metal sites, Fe(*2f*) and Fe(*1c*), are coordinated to symmetrically equivalent sulphurs and both these metal-coordinated tetrahedra are regular, consistent with Fe-tetrahedra in chalcopyrite and talnakhite.

The thermal parameters are listed as anisotropic U_{ij} and average isotropic B , in Table 2. Fig. 4 shows the thermal ellipsoids plotted using the program ORTEP (Johnson, 1965) at the 99% probability limit. The temperature factors are essentially isotropic and are in good agreement with the expected values (see Table 1). This provides a reasonable degree of confidence in the choice of Cu and Fe atoms for metals at *4n*, *4l*, *4i*, and *2f*, and to a lesser extent for metals of *1c*, *1b*, *1a*, and *1d*. It is difficult to say if the anisotropy associated with some of the atoms is significant or not. The thermal parameters are not well-determined because of several factors: the large proportion of very weak intensities, the dominance of sub-cell intensities, and the not insignificant least-squares correlation present in the refinement of a symmetric structure of this nature.

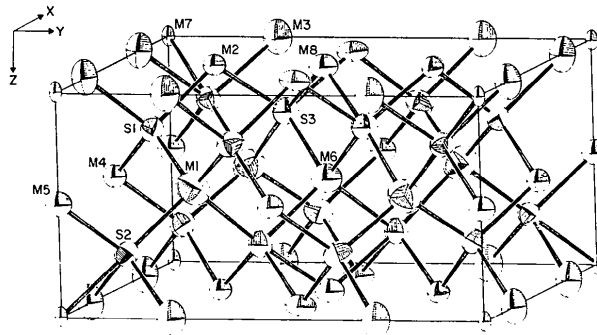


Fig. 4. Unit-cell model of mooihokite showing the thermal ellipsoids of the atoms, plotted at the 99% probability level.

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References

- BUSING, W. R. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 319–330. Copenhagen: Munksgaard.
- CABRI, L. J. (1973). *Econ. Geol.* **68**, 433–454.
- CABRI, L. J. & HALL, S. R. (1972). *Amer. Min.* **57**, 689–708.
- CABRI, L. J., HALL, S. R., SZYMANSKI, J. T. & STEWART, J. M. (1973). *Canad. Min.* **12**, 33–38.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1896.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- DONNAY, G., CORLISS, L. J., DONNAY, J. D. H., ELLIOTT, N. & HASTINGS, J. M. (1958). *Phys. Rev.* **112**, 1917–1923.
- GABE, E. J. & O'BYRNE, T. (1970). *Amer. Cryst. Assoc. summer meeting, Abstracts*. Paper A4.
- HALL, S. R. & GABE, E. J. (1972). *Amer. Min.* **57**, 368–380.
- HALL, S. R. & STEWART, J. M. (1973). *Acta Cryst.* **B29**, 579–586.
- HILLER, J. E. & PROBSTHAIN, K. (1956). *Z. Kristallogr.* **108**, 108–129.
- JOHNSON, C. K. (1965). *Fed. Sci. Tech. Info. Rep. ORNL-3794*.
- PAULING, L. & BROCKWAY, L. O. (1932). *Z. Kristallogr.* **82**, 188–194.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). *Univ. Maryland Comput. Sci. Tech. Rep.* TR-192.
- SZYMANSKI, J. T. (1973). *Z. Kristallogr.* Submitted for publication.
- TOMIIE, Y. & STAM, C. H. (1958). *Acta Cryst.* **11**, 126–127.
- TOWNSEND, M. G., HORWOOD, J. L., HALL, S. R. & CABRI, L. J. (1971). *17th Conf. Magn. and Magn. Mater. Abstr.* Paper 2H-13.