The crystal structure of high-temperature CuFe$_2$S$_3$*

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Abstract

The crystal structure of high-temperature CuFe$_2$S$_3$ has been determined from multiple sets of four-circle x-ray diffractometer data, refined to $R = 0.048$ (all data) and $R = 0.027$ (observed data only). This material is the direct product of the thermal transformation of cubanite, CuFe$_2$S$_3$ (orthorhombic, $Pnmn$). The cell data are: cubic, $F\bar{4}3m$, $a = 5.296$ Å, $Z = 4$. Larger crystals are always twinned about one of the [111] directions, but a small untwinned fragment was used in the analysis. There is complete disorder of Cu and Fe between the metal sites of the sphalerite-like cell, and both the 4$c$, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$, and 4$d$, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, sites of the space group are partially occupied by the metals.

Introduction

Natural orthorhombic cubanite, when heated above about 200°C transforms directly to a face-centred cubic polymorph (Cabrera et al., 1973). This transformation has so far proved irreversible in the laboratory. The material found in nature has always been orthorhombic, apart from one occurrence of the cubic form reported by Genkin et al.

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The crystal structure of high-temperature CuFe₂S₃ (1966), though their results suggest that further characterization of their material is warranted.

The transformation from orthorhombic cubanite to high-temperature CuFe₂S₂ has been reported as occurring via a tetragonal phase (YUND and KULLERUD, 1966). However, CABRI et al. (1973) have suggested that the tetragonal powder pattern was due to a mixture of the cubic CuFe₂S₃ and an exsolved tetragonal phase, which they considered to be chalcopyrite. Furthermore, the report of VAASJOKI (1971) that high-temperature CuFe₂S₂ exists as a hexagonal phase with c = 9.17 Å, can now be explained in terms of the pseudohexagonal, twinned cubic cell (CABRI et al., 1973). At present, therefore, there appear to be only two polymorphs of CuFe₂S₃: orthorhombic cubanite and cubic high-temperature CuFe₂S₃.

While orthorhombic cubanite has a structure that is closely related to the hexagonal wurtzite structure (BUERGER, 1947; SZYMAŃSKI, 1974), it has been proposed by FLEET (1970), on the basis of x-ray powder intensities and d values, that cubic CuFe₂S₃ has a sphalerite-like structure. He also suggested that the orthorhombic and cubic forms should have a structural relationship as do wurtzite and sphalerite. This relationship has been investigated further by CABRI et al. (1973), who have determined the orthorhombic-to-cubic transformation matrix and have given an explanation for the single [111] twin relationship usually present in crystals of cubic CuFe₂S₃.

**Experimental**

**Crystal data**

Source: Transformed from natural cubanite from Strathcona mine, Sudbury, Ontario. Supplied by Dr. L. J. CABRI.

Microprobe analysis: Identical to that of natural cubanite (SZYMAŃSKI, 1974).

Values in atomic %: Cu: 16.8(1), Fe: 33.3(2), S: 50.0(2).

Chemical composition: Cu₁₀Fe₂₀S₃₀.

Formula: CuFe₂S₃; Formula weight = 271.43.

Crystal system: Cubic.

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¹ As cubanite is an accepted mineralogical name for the naturally occurring orthorhombic species, the high-temperature cubic form will be referred to as high-temperature CuFe₂S₃. Strictly speaking, the latter is a member of specific composition of the cubic intermediate solid solution phase (CABRI, 1973).
Space group: $F\overline{4}3m$, cell dimension $a = 5.296(2)\,\text{Å}$ at 20°C, using $\lambda(MoK\alpha) = 0.70926\,\text{Å}$. 

$Z = 1\frac{1}{2}$, representing $(\text{Cu}_{13}\text{Fe}_{23})_4\text{S}_4$ per unit cell.

Systematic absences: $hk0, h + k, k + l, l + h = 2n + 1$.

$D_{\text{calc}} = 4.054(2)\,\text{g. cm}^{-3}$. $V = 148.58(9)\,\text{Å}^3$.

Linear absorption coefficient: $\mu(MoK\alpha) = 126.25\,\text{cm}^{-1}$.

Intensity data: 83 $hkl$ and 61 $hk0$ unique reflections obtained from averaging the data from 5 octants of reciprocal space containing 1670 reflections.

The high-temperature CuFe$_2$S$_3$ material was prepared by heating specimens of previously characterized cubanite in sealed quartz tubes for two days at 300°C, and subsequent quenching in icewater (CABRI et al., 1973). With one exception, all crystals examined were twinned with two components in equal proportion related by a (111) twin plane. The untwinned fragment was irregularly shaped, and approximately 0.05 mm across. This fragment was identified as a single crystal by x-ray precession techniques. Long exposures revealed only reflections which could be indexed on the basis of a face-centred cubic cell; no evidence of a supercell was found. The crystal was mounted in a general orientation on a Picker four-circle automatic diffractometer. The cell parameter and orientation matrix were obtained from a least-squares refinement of the $2\theta, \gamma$, and $\omega$ values (Busing, 1970) of the twenty-four 620 reflections, assuming a triclinic system. The deviation from the mean cell edge was half the quoted standard deviation, and the maximum deviation from orthogonality was 0.017°. The refined cell-edge, 5.296(2) Å, is in excellent agreement with values previously quoted in the literature, namely 5.294, 5.295 Å (SAWADA et al., 1962), and 5.2949(3) Å (FLEET, 1970).

Intensity data were collected using graphite-monochromated MoKα radiation in $\theta$-2$\theta$ scan mode, with a peak base width of 3.6°, increasing with 2$\theta$ to account for dispersion, a scan speed of 2°/min, and a background count of 60 sec on either side of the peak. Although the asymmetric dataset can be defined by the restriction that $h \geq k \geq l$, five complete octants of intensity data to a 2$\theta$ limit of 120° were collected, with 334 reflections per octant. Relative to the first arbitrary choice of the $a_1, a_2, a_3$ cubic axes, these were $hkl$, $hk0$, $hk0$, $hk0$, and $hkl$. A standard was measured every 50 reflections to monitor instrument stability and crystal alignment. No variation, beyond that statistically
expected, was found. Spherical absorption corrections were applied to the data. Within each octant, no systematic variation of intensity for reflections related by the Friedel $43m$ symmetry, was observed. The data were sorted into $hkl$ and $\bar{h}\bar{k}\bar{l}$ reflections, and within each Friedel-related group, the data were averaged and reduced to a unique data set. A total of 83 independent $hkl$ reflections were measured, in addition to 61 Friedel-related $\bar{h}\bar{k}\bar{l}$ reflections. Within these two groups, 55 and 39 reflections respectively, were considered as stronger than the observable threshold at the $10\%$ significance level, $I_{\text{net}} > 1.65\sigma(I_{\text{net}})$.

**Refinement**

The space group $F43m$ does not permit the assignment of copper and iron atoms to different sites within the limitation of 4 metal atoms/unit cell. As no evidence of a supercell was found, it must be presumed that the copper and iron atoms are disordered throughout the metal sites. The sulfur atoms were, therefore, placed at the $4a$ site, $000$, and the metal atoms at the $4c$ site, $\frac{1}{4} \frac{1}{4} \frac{1}{4}$. The scattering curves used were the $S^2$ curve of Tomilin and Stamat (1958), and for the metals, an arithmetic mean of the $Cu^{1+}$, $Fe^{2+}$ and $Fe^{3+}$ curves of Cromer and Mann (1968). A discussion on the use of ionic $f$ curves for such minerals has already been given (Szymanski, 1974). The anomalous dispersion corrections (weighted-mean correction for the metals) were taken from Cromer and Libermann (1970). All the structural computations were performed using the X-RAY system of programs (Stewart et al., 1972). The refinements were performed by a full-matrix least-squares procedure with isotropic thermal parameters (as required by the $43m$ point symmetry of sites $4a$ and $4c$), and an isotropic extinction parameter (Larson, 1970). Only the 83 $hkl$ reflections were used in the initial structure refinement. This included the reflections stronger than the $10\%$ significance threshold ("observed" reflections) and those less than the threshold ("less-than" reflections). The refinement converged to $R = (\Sigma \left| F_o \right| - \left| F_c \right|)/\Sigma \left| F_o \right| = 0.102$. A difference synthesis showed a prominent peak at the "inverse" tetrahedral site $4d$, $\frac{1}{4} \frac{3}{4} \frac{1}{4}$, and a negative peak at the metal site $4c$, $\frac{1}{4} \frac{1}{4} \frac{1}{4}$. This was interpreted as being due to disorder of the metal atoms between the two structurally-equivalent tetrahedral sites. The metal occupancy of the $4d$ site was included as a least-squares parameter, and the occupancy of the $4c$ site was adjusted between cycles. The temperature factors of the metals at the two sites were refined, but kept equal. The Friedel-related $hkl$ reflections were then included in the calculations in order to distinguish
the "absolute configuration" of the structure relative to the $a_1$, $a_2$, $a_3$ axes chosen at the time of data collection2.

It was found that the disagreement factors for the two models (one with metals mainly at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, the other with metals mainly at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$) were $R = 0.071$ and 0.048, respectively, using all 144 data. Considering only the 94 observed reflections, the disagreement factors were $R = 0.050$, and 0.027, respectively. Consequently, the axial system was changed so that the metal, or in this case, the majority of the metal atoms, would be in the $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ position of the sphalerite-like cell.

Table 1. Measured and calculated structure factors (×10). The structure factors marked with an asterisk were considered unobserved at the 10% significance level, those which were derived from a negative net intensity were given a value of zero.

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>$F_{\text{hkl}}$</th>
<th>$F_{\text{calc}}$</th>
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<td>2</td>
<td>539 062 062</td>
<td>536 054 054</td>
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<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>100 000 000</td>
<td>100 000 000</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>150 150 150</td>
<td>149 149 149</td>
</tr>
</tbody>
</table>

Table 2. Final atomic parameters for high-temperature CuFe$_2$S$_3$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>Position</th>
<th>Occupancy</th>
<th>Isotropic temperature factor, ( B = 8 \pi^2 U )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>4a</td>
<td>0 0 0</td>
<td>1.0</td>
<td>1.42(3) ( \AA^2 )</td>
</tr>
<tr>
<td>M*</td>
<td>4c</td>
<td>$\frac{1}{4} \frac{1}{4} \frac{1}{4}$</td>
<td>0.908</td>
<td>1.32(2)</td>
</tr>
<tr>
<td>M</td>
<td>4d</td>
<td>$\frac{1}{2} \frac{1}{2} \frac{1}{2}$</td>
<td>0.094(3)$^b$</td>
<td>1.32</td>
</tr>
</tbody>
</table>

$a$ The metal M represents the disordered composition (Cu$_{1/3}$ Fe$_{2/3}$).

$b$ Refined parameters; corresponding parameter for the other M is adjusted accordingly.

Strictly speaking, there is no question of absolute configuration, because the inverse enantiomer, with the metal site at $-\frac{1}{2} -\frac{1}{2} -\frac{1}{2}$, can be obtained from the starting enantiomer with the metal site at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, by redefining $a_1$, $a_2$, $a_3$ as $-a_1$, $-a_2$, $-a_3$. The anomalous scattering component of the structure factors can serve to distinguish between the two possible orientations of the model though structurally these are identical.
At convergence, the 4c and 4d sites had occupancies of 0.906 and 0.094(4), respectively. A final difference synthesis showed no significant residual features. The list of measured and calculated structure factors is set out in Table 1. All data are included at the values obtained from the mean $J_{\text{net}}$, and those which are considered as unobserved at the 10% significance level are denoted by an asterisk. The refinement parameters are given in Table 2.

**Discussion**

The structure of high-temperature CuFe$_2$S$_3$ is based upon a cubic close-packed matrix of sulfur atoms, with the metal atoms located in the tetrahedral interstices of the matrix. Most of the (Cu$_{1/3}$,Fe$_{2/3}$) metal atoms in the sphalerite-like cell occupy one set of sites, with the remainder (about 9%0) in the inverse set. The idealized structure, with the metal atoms in only one set of tetrahedral sites is illustrated in Fig. 1. The “inverse” positions are obtained by inversion through the sulfur-atom positions.

![Diagrammatic representation of the sphalerite-like cell of CuFe$_2$S$_3$. The large spheres represent the sulfur atoms and the small spheres the disordered (Cu$_{1/3}$,Fe$_{2/3}$) atoms. The metal atoms are drawn in only one of the partially occupied tetrahedral sites, 4c. The other position, 4d, is obtained from the 4c position by inversion at each sulfur atom. The origin of the diagram is in the upper corner.](image-url)
The metal-sulfur bond length is 2.293(1) Å and the sulfur-sulfur distance is 3.745(1) Å. The metal-sulfur distance is between the Cu—S and the Fe—S distances, 2.302(1) and 2.257(1) Å, recently found in chalcopyrite (Hall and Stewart, 1973), and in the middle of the range of metal-sulfur distances found in cubanite (Szymański, 1974).

There are two possible structural interpretations of the partial occupancy in the 4c and 4d disordered-metal sites. Though it may be expressed as an average 9% occupancy of the 4d sites and 91% occupancy of the 4c sites, this may be interpreted in one of two ways: either as a simultaneous occupation of both sites in the same cell, or as the existence of domains with fully occupied 4c (or 4d) disordered-metal sites related to each other by inversion centres. In the latter case, the proportion of domains is likely to be a property of the particular crystal examined. In both interpretations, the cubic close-packed sulfur matrix would be continuous.

If the former interpretation is accepted, there must exist occasional metal–metal distances between adjacent tetrahedral sites of 2.648(1) Å. This distance is much closer than the closest Fe–Fe distance in cubanite 2.804(1) Å (Szymański, 1974). However, in copper-iron sulfide minerals that contain interstitial metal atoms, such as talmakhite (Hall and Gabe, 1972), metal-metal distances of 2.57, 2.65 and 2.72 Å have been reported. Furthermore, in argentian pentlandite (Hall and Stewart, 1973) there exists a cube of (Ni,Fe) atoms of side 2.65 Å. It appears, then, that such a distance between adjacent tetrahedrally coordinated metals is not particularly unfavorable energetically in a face-centred, cubic sulfur matrix. If the second interpretation is given to the 9% occupancy of the 4d sites, then the close approach of 2.648 Å will occur between metal atoms only along the domain interfacial boundaries.

Cabrè (1973) has indicated that within two months of quenching high-temperature CuFe$_2$S$_3$, the material gives a somewhat changed x-ray powder pattern compared with the original pattern of the newly quenched material. A blurring of lines and an appearance of new lines has been observed. The crystal used in this analysis was mounted on the diffractometer within two weeks of transformation, and data collection was complete within another two weeks. Although no evidence of new phases, or of gradual transformation, was found in this analysis, it should be noted that the temperature factors of atoms in high-temperature CuFe$_2$S$_3$ are significantly higher than in natural cubanite (Szymański, 1974). For natural cubanite, \( B(S) = 0.96 \, \text{Å}^2 \) and the
weight mean for the metals $B(M) = 1.05 \AA^2$. For high-temperature CuFe$_2$S$_3$, the values are $B(S) = 1.42 \AA^2$, $B(M) = 1.32 \AA^2$. These values are consistent with the unstable nature of the quenched high-temperature phase and the ready mobility of the metal atoms, which is necessary for the exsolution of the tetragonal phase from high-temperature CuFe$_2$S$_3$ (CABRI et al., 1973).

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**References**


L. J. CABRI (1973), New data on phase relations in the Cu–Fe–S system. Econ. Geol. 68, 443–454.


