Zeitschrift für Kristallographie, Bd. 140, S. 240–248 (1974)

The crystal structure of high-temperature $CuFe_2S_3$*

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(Received 16 July 1973)

Auszug

Die Kristallstruktur der Hochtemperaturform von $CuFe_2S_3$ wurde aus Daten nach Messungen mit dem Vierkreis-Diffraktometer bestimmt und bis zu $R = 0{,}027$ (aus beobachteten Interferenzen allein) verfeinert; $R = 0{,}048$ für alle möglichen Reflexe. Die Substanz wurde durch Erhitzen von Cubanit erhalten. Die Gitterkonstante ist $a = 5{,}296$ Å, die Raumgruppe $F\bar{4}3m$, $Z = 4/3$. Größere Kristalle sind stets nach einer $\langle 111 \rangle$-Richtung verzwillingt; für die Untersuchung konnte jedoch ein kleines unverzwillingtes Bruchstück verwendet werden. Die Cu- und Fe-Atome sind völlig ungeordnet auf die zwei, von ihnen nur teilweise besetzten, Punktlagen $4c$, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ und $4d$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ der zinkblendeähnlichen Zelle verteilt.

Abstract

The crystal structure of high-temperature $CuFe_2S_3$ 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, $CuFe_2S_3$ (orthorhombic, *Pcmn*). The cell data are: cubic, $F\bar{4}3m$, $a = 5.296$ Å, $Z = 1\frac{1}{3}$. 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 $4c$, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, and $4d$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$, sites of the space group are partially occupied by the metals.

Introdution

Natural orthorhombic cubanite, when heated above about 200 °C transforms directly to a face-centred cubic polymorph (Cabri *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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* Mineral Research Program — Sulphide Research Contribution No. 79.

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(1966), though their results suggest that further characterization of their material is warranted.

The transformation from orthorhombic cubanite to high-temperature $CuFe_2S_2$ 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 $CuFe_2S_3$ and an exsolved tetragonal phase, which they considered to be chalcopyrite. Furthermore, the report of Vaasjoki (1971) that high-temperature $CuFe_2S_3$ 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 $CuFe_2S_3$: orthorhombic cubanite and cubic high-temperature $CuFe_2S_3$ [1].

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 $CuFe_2S_3$ 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 $CuFe_2S_3$.

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 $^0/_0$: Cu: 16.8(1), Fe: 33.3(2), S: 50.0(2).

Chemical composition: $Cu_{1.01}Fe_{2.00}S_{3.00}$.

Formula: $CuFe_2S_3$; 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* $CuFe_2S_3$. Strictly speaking, the latter is a member of specific composition of the cubic intermediate solid solution phase (Cabri, 1973).

Space group: $F\bar{4}3m$, cell dimension $a = 5.296(2)$ Å at 20 °C, using $\lambda(\mathrm{Mo}K\alpha_1) = 0.70926$ Å.

$Z = 1\frac{1}{3}$, representing $(\mathrm{Cu}_{1/3}\mathrm{Fe}_{2/3})_4\mathrm{S}_4$ per unit cell.

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

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

Linear absorption coefficient: $\mu(\mathrm{Mo}K\alpha) = 126.25$ cm^{-1}.

Intensity data: 83 hkl and 61 $\bar{h}kl$ unique reflections obtained from averaging the data from 5 octants of reciprocal space containing 1670 reflections.

The high-temperature $\mathrm{CuFe_2S_3}$ 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 2θ, χ, and ω 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 Mo$K\alpha$ radiation in θ-2θ scan mode, with a peak base width of 3.6 °, increasing with 2θ 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 data set can be defined by the restriction that $h \geq k \geq l$, five *complete* octants of intensity data to a 2θ 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, $h\bar{k}\bar{l}$, $\bar{h}kl$, $hk\bar{l}$, and $\bar{h}\bar{k}\bar{l}$. 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 $\bar{4}3m$ symmetry, was observed. The data were sorted into hkl and $\bar{h}kl$ 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 $\bar{h}kl$ 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 $F\bar{4}3m$ 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, 0 0 0, 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 Tomiie and Stam (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 (Szymański, 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 $\bar{4}3m$ 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 $R = (\Sigma \| F_o| - |F_c\|)/\Sigma |F_o| = 0.102$. A difference synthesis showed a prominent peak at the "inverse" tetrahedral site $4d$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$, 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 $\bar{h}kl$ reflections were then included in the calculations in order to distinguish

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

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
1 1 1	846	837	5 3 1	294	291	6 6 6*	0	41	8 4 0	194	192	9 5 1	83	81	10 6 2*	14	29
2 0 0	442	403	3	255	260	7 1 1	207	203	2*	44	53	3	63	65	4	64	60
2 2 0	1002	1007	5 5 1	218	220	7 3 1	195	188	4	149	146	5*	52	56	10 8 0*	18	22
2	306	307	3	175	172	3	148	148	8 6 0*	33	45	9 7 1*	41	51	11 1 1	52	57
3 1 1	586	573	5	139	139	7 5 1	126	127	2	130	127	3*	54	49	11 3 1*	42	56
3 3 1	465	466	6 0 0	124	120	3	120	121	4*	31	38	5*	12	35	3*	46	45
3	349	356	6 2 0	429	425	5	91	84	6	81	77	9 9 1*	0	34	11 5 1*	29	40
4 0 0	786	778	2	96	98	7 7 1	91	92	8 8 0	90	87	10 0 0*	21	45	3*	37	39
4 2 0	226	213	6 4 0	77	83	3	83	74	2*	24	32	10 2 0	123	127	12 0 0	65	63
2	607	625	2	306	303	5*	56	63	4	71	68	2*	29	41	12 2 0*	27	27
4 4 0	504	511	4	41	65	7*	17	40	6*	25	22	10 4 0*	28	38	2	57	60
2	118	120	6 6 0	229	222	8 0 0	258	259	9 1 1	110	121	2	92	98	12 4 0*	49	53
4	348	357	2*	46	59	8 2 0*	54	65	9 3 1	89	96	4*	19	32	2*	31	22
5 1 1	386	377	4	174	167	2	226	222	3	87	92	10 6 0	86	77			
-1 1 1	804	812	-5 5 1	198	203	-7 3 3	164	161	-8 6 2	135	127	-9 5 5*	43	51	-11 3 1*	47	51
-2 2 2	299	307	3	193	188	-7 5 1	143	139	4*	50	38	-9 7 1*	56	56	3*	52	49
-3 1 1	604	594	5	121	127	3	106	110	6	89	77	3*	33	45	-11 5 1*	44	44
-3 3 1	438	444	-6 2 2	101	98	5	95	92	-8 8 2*	42	32	5*	43	39	3*	36	35
3	372	377	-6 4 2	304	303	-7 7 1	76	84	4	68	68	-9 9 1*	0	31	-12 2 2	76	60
-4 2 2	598	624	4	69	65	3	86	81	6*	38	22	-10 2 2*	21	41	-12 4 2*	30	22
-4 4 2	120	120	-6 6 2*	61	59	5*	46	57	-9 1 1	112	110	-10 4 2	89	98			
4	341	357	4	170	167	7*	27	44	-9 3 1	104	105	4*	24	32			
-5 1 1	361	356	6*	20	41	-8 2 2	219	222	3	83	84	-10 6 2*	30	29			
-5 3 1	311	311	-7 1 1	227	220	-8 4 2*	54	53	-9 5 1	77	74	4	55	60			
3	236	242	-7 3 1	177	172	4	151	146	3	76	71	-11 1 1*	60	63			

Table 2. *Final atomic parameters for high-temperature* $CuFe_2S_3$

Atom	Site	Position	Occupancy	Isotropic temperature factor, $B = 8\pi^2 U$
S	4*a*	0 0 0	1.0	1.42(3) Å^2
M[a]	4*c*	$\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$	0.906	1.32(2)
M	4*d*	$\frac{3}{4}$ $\frac{3}{4}$ $\frac{3}{4}$	0.094(3)[b]	1.32

[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.

the "absolute configuration" of the structure relative to the a_1, a_2, a_3 axes chosen at the time of data collection[2].

It was found that the disagreement factors for the two models (one with metals mainly at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, the other with metals mainly at $\frac{3}{4}\frac{3}{4}\frac{3}{4}$) 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 $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ position of the sphalerite-like cell.

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[2] Strictly speaking, there is no question of absolute configuration, because the inverse enantiomer, with the metal site at $-\frac{1}{4}$, $-\frac{1}{4}$, $-\frac{1}{4}$, can be obtained from the starting enantiomer with the metal site at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, by redefining a_1, a_2, a_3 as $-a_1$, $-a_3$, $-a_2$. 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 4*c* and 4*d* 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 I_{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 $CuFe_2S_3$ 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%) 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.

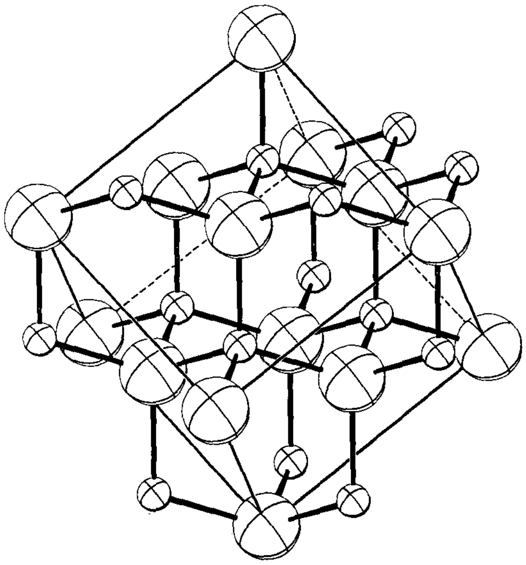

Fig. 1. Diagrammatic representation of the sphalerite-like cell of $CuFe_2S_3$. The large spheres represent the sulfur atoms and the small spheres the disordered $(Cu_{1/3},Fe_{2/3})$ atoms. The metal atoms are drawn in only one of the partially occupied tetrahedral sites, 4*c*. The other position, 4*d*, is obtained from the 4*c* position by inversion at each sulfur atom. The origin of the diagram is in the upper corner

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 4*c* and 4*d* disordered-metal sites. Though it may be expressed as an average 9% occupancy of the 4*d* sites and 91% occupancy of the 4*c* 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 4*c* (or 4*d*) 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 talnakhite (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 4*d* sites, then the close approach of 2.648 Å will occur between metal atoms only along the domain interfacial boundaries.

CABRI (1973) has indicated that within two months of quenching high-temperature $CuFe_2S_3$, 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 $CuFe_2S_3$ are significantly higher than in natural cubanite (SZYMAŃSKI, 1974). For natural cubanite, $B(S) = 0.96$ Å^2 and the weighted mean for the metals $B(\mathrm{M}) = 1.05$ Å^2. For high-temperature $CuFe_2S_3$, the values are $B(\mathrm{S}) = 1.42$ Å^2, $B(\mathrm{M}) = 1.32$ Å^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 $CuFe_2S_3$ (Cabri *et al.*, 1973).

Acknowledgements

The author is grateful to Dr. S. R. Hall, of this Division for much useful help and discussion in the work and for critical reading of the manuscript. Thanks are due to Dr. L. J. Cabri, of this Division, for preparing the high-temperature $CuFe_2S_3$ crystal used in this analysis, and for the microprobe work done on the transformed cubanite specimens. The diagram was prepared using the computer program ORTEP (Johnson, 1965).

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