

Refinement of the crystal structure of cubanite and polymorphism of CuFe_2S_3

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Auszug

Die Kristallstruktur eines Cubanits von der Strathcona Mine, Ontario, wurde bis zu $R = 0,107$ als Endwert verfeinert. Die für die Cubanitstruktur eigentümliche Anordnung der Fe-Atome beiderseits der gemeinsamen Kante der sie umgebenden Tetraeder deutet auf einen gewissen Grad von σ -Bindung zwischen den e -Elektronen der Metalle hin. Die gefundenen Deformationen der Koordinationspolyeder sind jedoch nicht ganz im Einklang mit diesem Modell. Über den Ursprung des schwachen Ferromagnetismus werden im Lichte der neuen Ergebnisse und der modernen Theorie des Magnetismus Betrachtungen angestellt.

Unter niederen Drucken wandelt sich Cubanit schon bei Temperaturen unterhalb von 220°C in die kubische Modifikation um. Diese Form hat, wie eine Untersuchung mit Hilfe von nach der Pulvermethode gewonnenen Intensitäten zeigt, Zinkblendestruktur.

Abstract

The crystal structure of cubanite has been refined using single-crystal x-ray intensity data from material from the Strathcona Mine, Sudbury District, Ontario. A value of the conventional residual index of 0.107 for refinement of positional, scale and isotropic thermal parameters was obtained. The structural peculiarity of cubanite, in which the Fe atoms are opposed across shared tetrahedral coordination edges, suggests some degree of σ -bond formation between the metal e orbitals, although consideration of the distortion observed in the structure is not entirely in accord with this model. Some observations are made on the origin of the weak ferromagnetism in the light of the new data and modern magnetic theory. Experiments on the stability of cubanite show that at low pressure it inverts to the cubic form at less than 220°C . A structural investigation of the cubic modification, based on x-ray powder intensity data, demonstrates that it has the sphalerite structure.

Introduction

Cubanite, CuFe_2S_3 , is a naturally occurring compound frequently associated in accessory amounts with chalcopyrite, pyrrhotite and pentlandite, and noteworthy because it is weakly ferromagnetic. Its

Table 1. *Positional parameters of AZAROFF and BUEGER*

	<i>x</i>	<i>y</i>	<i>z</i>
Cu in 4 <i>c</i>	0.583	$\frac{1}{4}$	0.127
S(1) in 4 <i>c</i>	0.587	$\frac{1}{4}$	0.762 ₅
Fe in 8 <i>d</i>	0.412 ₅	0.412	0.634
S(2) in 8 <i>d</i>	0.413	0.416 ₅	0.274

crystallographic properties have been investigated by BUEGER (1945, 1947): it is orthorhombic, space group *Pcmm*, with $a = 6.46$, $b = 11.17$, $c = 6.234$ Å, 4 formula units per unit cell. The structure is based upon a hexagonal close-packed network of S atoms with the cations in ordered, tetrahedral sites; the Cu atoms and 1/3 of the S atoms occupy the equipoint 4*c* (mirror planes), and the Fe atoms and remaining 2/3 of the S atoms are in the general positions, 8*d*. It can be regarded, as described by BUEGER, as made up of slices of the wurtzite structure parallel to (010) and $b/2$ wide, joined to identical but inverted slices by means of the sharing of one of the edges of each Fe coordination tetrahedron (Fig. 1). The provisional positional parameters were refined later by AZAROFF and BUEGER (1955) by Fourier difference syntheses: the values obtained are given in Table 1.

The thermal stability was investigated independently by YUND and KULLERUD (1966) and SAWADA *et al.* (1962). According to the former, cubanite, on heating under vacuum, inverts to a form of

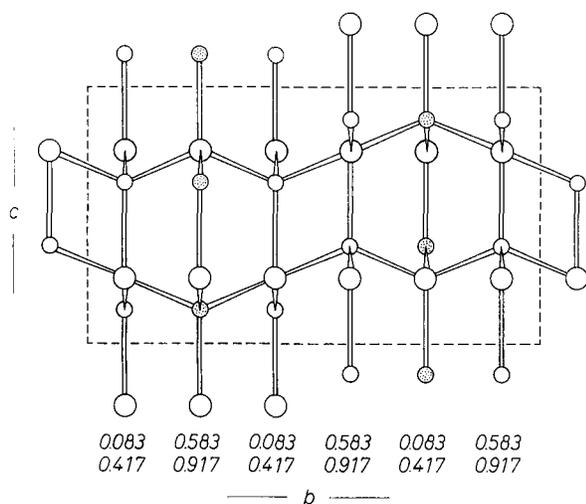


Fig. 1. The ideal structure of cubanite. S: large open circles; Fe: small open circles; Cu: small stippled circles; the *x* coordinates are indicated

CuFe_2S_3 reported to be tetragonal at 213°C and the tetragonal form, in turn, inverts to a cubic modification at $252 \pm 5^\circ\text{C}$: both reactions were not reversed about the transformation temperatures. SAWADA *et al.* reported that natural cubanite inverts, irreversibly, to a cubic phase at about 270°C .

The present study of the structure and crystal chemistry of cubanite and the polymorphism of CuFe_2S_3 was undertaken after acquisition of suitable natural material.

Refinement of the cubanite structure

A natural specimen in the form of twinned single crystals 4–6 mm in longest dimension was used in the investigation: it had been obtained from a vug in the Strathcona Mine, Sudbury District, Ontario. The composition was verified by electron microprobe analysis as essentially stoichiometric and Co and Ni, the most likely minor elements, were not detectable. The lattice parameters, obtained using a Jagodzinski focussing powder camera by a procedure reported elsewhere (FLEET, 1968), are $a = 6.4679(5)$, $b = 11.1201(8)$, $c = 6.2336(4)$ Å—the standard deviations are indicated in parentheses. These values agree quite favourably with BUERGER's data, which were obtained using a precision back-reflection Weissenberg apparatus.

A crystal fragment, roughly triangular prismatic in shape, with a longest dimension of about 0.1 mm and a volume of $0.2 \cdot 10^{-3}$ mm³ was selected. The small size was considered desirable to reduce the effects of absorption and the possibility of having a twinned fragment. Precession and Weissenberg studies showed clearly that the fragment chosen was not twinned, that it was not polycrystalline and that the reflection spots were sharp and distinct. The x-ray intensity data were taken on a Picker facs 1 four-circle diffractometer system at the Manned Space Craft Centre, Houston. All reflections with $2\theta \leq 80^\circ$ were measured with Zr-filtered $\text{MoK}\alpha$ ($\lambda = 0.7107$ Å) radiation using the 2θ -scan technique: 10-second stationary background counts and peak base widths of $1^\circ 2\theta$ (uncorrected for dispersion). The resulting data were processed by a data correction routine which removed space-group extinctions and corrected for background, Lorentz and polarization effects and absorption, and assigned standard deviations to the corrected data based on the summed variances of the counting rates of the peaks and associated backgrounds. Transmission factors for the absorption correction were calculated by Gaussian integration

of the volume elements with a value for the linear absorption coefficient of 126.3 cm^{-1} . The data included a large number of weak and "unobserved" reflections: each reflection whose intensity was less than the background plus two standard deviations was given zero intensity.

A full-matrix least-squares refinement was effected using program RFINE (L. FINGER, Geophysical Laboratory, Washington). The scattering curves for Fe^{2+} and Cu^{2+} were taken from CROMER and MANN (1968) and that for S^{2-} computed for a nine-parameter fit from data in the *International tables for x-ray crystallography*, Vol. III with a program slightly modified from one kindly made available by D. T. CROMER, University of California, Los Alamos; the anomalous-dispersion coefficients of CROMER (1965) for S, Fe and Cu were included. The starting values for the refinement were the provisional positional parameters of BUERGER (1947) (the author was not aware of the work of AZAROFF and BUERGER at this time), isotropic temperature factors of 1.0 and ordered cation occupancies. Reflections with $F_{\text{obs}} = 0.0$ were excluded from the refinement; of the 1432 reflections not excluded by space-group considerations, only 587 were used. The positional parameters and scale factor were refined initially, then the isotropic temperature parameters were included. At this stage the cation-site occupancies were refined from a random-distribution hypothesis.

Each stage required three or four cycles for convergence. The site refinement suggested that the structure was ideally ordered. The final values for the weighted and conventional residual indices are 0.123 and 0.107 respectively. The values of the residual indices reflect the large number of weak reflections in the reflection data used. For the value of the conventional residual index for the isotropic refinement reported, the residual indices were calculated for eight equal intervals of F_{obs} for all the reflections used: the value for the lowest interval was 0.185 and that for the average of the other seven intervals was 0.072. A similar analysis in terms of ranges of $(\sin^2 \theta)/\lambda^2$

Table 2. *Positional parameters and temperature factors for the isotropic refinement*

	S(1)	S(2)	Fe	Cu
<i>x</i>	0.5693(18)	0.4038(10)	0.4125(06)	0.5792(09)
<i>y</i>	$\frac{1}{4}$	0.4137(09)	0.4131(03)	$\frac{1}{4}$
<i>z</i>	0.7595(10)	0.2672(07)	0.6372(05)	0.1205(07)
<i>B</i>	0.637(143)	0.837(089)	0.806(045)	1.221(075)

Table 3. Observed and calculated structure factors

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				
0	0	2	131	164	1	8	9	20	25	2	4	6	15	19	3	4	6	86	89	5	15	0	79	40	7	15	3	58	58				
			4	84	96	1	7	2	12	14			7	14	14			8	27	31			3	53	55	2	10	1	30	33			
			6	32	35				4	14	0	2	5	1	85	81			3	3	0	245	317			5	54	54	2	27	24		
			8	100	111				5	17	15			2	60	55			1	10	3			5	14	1	18	18	3	38	37		
			10	41	44	1	6	1	37	29			3	85	78			2	107	107			3	16	19	6	23	25	6	23	25		
0	1	2	160	166				2	26	23			5	27	25			3	14	7			5	12	1	18	18	7	9	0	72	67	
			4	13	10				3	62	54			6	39	39			4	68	69			5	10	1	60	46	2	33	29		
			6	105	105				4	12	7			7	29	17			5	12	8			2	28	30	3	67	62	5	65	60	
			8	34	33				5	18	17			9	27	28			6	29	30			3	54	53	5	65	60	1	28	28	
0	2	0	26	23				6	27	26			0	140	158			8	93	96			6	29	26	7	8	2	29	17	20		
			2	14	15				7	16	19			1	37	39			10	38	39			5	9	0	69	70	2	29	17	20	
			4	14	10				8	25	27			2	52	46			3	2	108	121			1	14	11	5	33	29	6	17	17
			6	26	29	1	5	0	15	7			3	155	156			4	10	10			2	28	25	2	28	25	5	6	17	17	
0	3	2	57	53				3	26	31			4	37	31			6	80	85			3	95	93	7	7	0	19	15	35	35	
			4	18	24				5	13	6			5	139	138			8	26	29			4	19	17	7	6	1	19	9	9	
			6	52	48				6	17	10			6	15	15			7	1	0	11	4			5	88	88	2	16	20	20	20
			8	54	54				7	14	9			8	48	45			2	13	15			8	26	29	5	7	10	5	31	20	
0	4	2	18	21				1	4	1	120	112			9	18	20			5	13	17			5	8	1	60	6	18	32	32	
			4	10	2				2	82	74			10	20	18			6	22	26			2	27	28	7	4	1	44	43	43	
			6	29	28				3	116	107			1	88	84			3	11	15			3	16	40	2	4	1	34	29	29	
0	5	2	124	120				5	33	32			2	6	6	36			3	0	2	41	46			6	19	25	3	49	46	46	
			6	84	83				6	55	51			3	93	86			5	11	17			5	7	0	12	24	7	3	0	94	91
			8	27	25				7	32	24			4	11	4			4	19	20			5	14	24	4	3	0	94	91	91	
0	6	0	277	318				8	21	18			5	27	23			6	46	45			5	6	1	27	28	1	16	19	19	19	
			2	122	109				9	33	24			6	43	42			8	3	42			2	17	5	2	3	2	42	39	39	
			4	74	66				11	30	33			7	25	21			4	0	0	143	156			3	45	48	3	85	82	82	
			6	27	32	1	3	0	61	213			8	16	14			1	38	45			5	5	15	13	5	14	16	16	16	16	
			8	92	97				1	51	47			9	29	30			2	61	58			3	5	3	18	5	5	81	77	77	
			10	35	39				2	82	70			0	17	27			3	129	147			5	4	1	67	65	8	37	34	34	
0	7	2	129	122				3	187	192			2	8	8	22			4	32	29			2	62	63	7	2	2	38	42	42	
			6	94	92				4	46	42			4	13	1			5	121	129			3	69	69	2	28	27	27	27	27	
			8	33	33				5	165	161			1	28	25			6	18	14			5	21	18	3	42	43	43	43	43	
0	8	0	32	34				6	22	17			2	13	10			8	30	48			6	33	34	5	16	16	16	16	16		
			4	17	9				8	59	54			3	47	46			9	21	19			7	20	19	6	28	25	25	25	25	
			6	20	22				9	24	21			5	14	14			10	19	21			9	25	25	7	0	2	10	23	23	
0	9	2	50	50				10	24	32			6	18	19			4	1	77	83			5	3	0	96	100	3	31	23	23	
			4	17	13				11	18	21			2	10	2			2	54	54			1	19	26	2	12	1	12	12	12	
			6	42	37	1	2	1	118	115			5	17	22			3	77	81			2	38	32	8	0	0	57	52	52	52	
			8	40	41				2	88	74			1	59	58			5	29	27			3	124	129	3	4	1	19	15	15	
0	10	2	16	17				3	116	105			2	25	26			6	43	42			4	25	26	3	7	7	7	7	7	7	
			6	19	20				4	14	5			3	41	38			7	20	20			5	11	118	4	16	17	17	17	17	
0	11	2	57	53				5	41	34			5	14	13			9	25	29			8	36	37	5	7	6	5	76	76	76	
			6	48	47				6	54	48			6	22	23			5	2	1	10	4			9	16	21	8	2	24	24	24
0	12	0	171	171				7	18	22			0	81	77			9	16	31			5	2	1	62	63	8	1	1	34	36	36
			4	37	29				8	18	15			2	37	33			4	3	1	28	20			2	39	44	2	23	25	25	25
			6	20	22				11	27	30			4	18	14			2	22	29			3	62	65	3	6	3	37	40	40	
			8	68	67	1	1	0	15	11			8	32	31			3	49	41			5	22	19	8	3	1	21	23	23	23	
0	13	2	71	71				2	66	60			6	49	47			4	11	2			6	28	33	3	3	3	3	3	3	3	
			6	60	65				5	10	6			2	34	31			6	26	37			7	16	17	8	5	2	28	28	28	
			8	25	26				7	13	12			3	55	54			7	15	20			5	1	0	10	35	3	34	31	31	
0	14	0	21	27				1	0	1	45	43			6	27	29			8	26	32			4	11	7	8	6	0	49	45	45
0	15	2	21	18				2	28	32			7	17	16			4	4	12	6			5	0	1	30	33	2	22	14	14	14
			6	26	24				3	67	70			2	14	18			4	5	1	65	65			2	14	15	3	7	7	7	7
0	16	0	44	19				4	15	11			2	15	15			2	45	40			3	48	37	8	7	1	33	33	33	33	
0	17	2	19	20				5	21	21			2	15	7			3	62	62			5	15	16	2	2	2	2	2	2	2	
0	18	0	82	86				6	27	30			3	27	27			5	27	22			6	16	1	3	3	3	3	3	3	3	
			5	40	37				7	18	22			0	38	39			6	35	32			8	18	0	8	8	0	3	26	26	26
0	19	2	35	36				8	28	31			1	18	15			7	18	15			6	0	0	173	194	8	4	1	17	18	18
			1	18	3	17	18		11	26	30			2	19	1			9	22	25			1	14	5	3	1	29	30	30	30	
1	16	1	36	35				2	0	160	198			3	27	31			4	6	0	126	125			2	77	73	8	11	1	17	17
			2	23	24				1	41	46			3	42	44			1	31	28			3	15	10	7	17	18	18	18	18</	

showed that the residual indices were distributed evenly over all eight intervals. The structure, and the refinement of it, were checked by F_{obs} and $F_{\text{obs}} - F_{\text{calc}}$ Fourier syntheses. No peaks other than those associated with the known structure were detected. However, shifts of $+0.01$ were suggested for the x parameters of S(1) and S(2). These shifts were applied but the structure refined back to the original parameters within two cycles.

The final values for the positional parameters and isotropic temperature factors ($B = 8\pi^2\bar{u}^2$) and associated standard deviations (in parentheses) are given in Table 2; the observed and calculated structure factors are given in Table 3. The positional parameters are, in general, quite similar to those of AZAROFF and BUERGER, but the x parameters of S(1) and S(2) differ significantly, being respectively 0.018 and 0.009 lower than the equivalent data of AZAROFF and BUERGER. These discrepancies are similar to the parameter shifts indicated by the difference Fourier, above. The Fourier and least-squares refinements, then, converge on different values for these parameters: presumably, this is a reflection of the higher symmetry of the close-packed S atoms. During the least-squares refinement the x parameters of S(1) and S(2) were reset with shifts in excess of those indicated by the difference Fourier. The refinement converged on a local minimum giving a value for the conventional residual index greater than 0.13.

An attempt was made to refine the structure using anisotropic thermal parameters. The refinement would not converge and gave a negative value to β_{11} of S(1). The correlation coefficients between the β_{11} and x parameters of S(1) and S(2) were large, again reflecting the pseudosymmetry of the S atoms. For this reason the thermal parameters of S(1) were constrained to equal the equivalent parameters of S(2). The refinement then converged although the values of β_{11} for S(1) and S(2) were still quite low. The values for the weighted and conventional residual indices are 0.120 and 0.103 respectively.

Table 4. *Positional and temperature parameters for the anisotropic refinement*

	S(1)	S(2)	Fe	Cu
x	0.5652(24)	0.4027(10)	0.4131(06)	0.5797(09)
y	$\frac{1}{4}$	0.4137(09)	0.4131(03)	$\frac{1}{4}$
z	0.7595(11)	0.2667(07)	0.6372(05)	0.1207(06)
B_{11}	0.256(197)	0.256(197)	0.987(096)	1.324(151)
B_{22}	0.835(116)	0.835(116)	0.564(106)	1.235(167)
B_{33}	0.987(102)	0.987(102)	0.857(081)	1.065(136)

According to the procedure for testing weighted residuals (HAMILTON, 1965), the hypothesis that all the atoms vibrate isotropically can be rejected only the 0.010–0.025 significance levels: the isotropic data is preferred and is used in the following sections. The values for the positional parameters and anisotropic temperature parameters (converted to the same units as the isotropic factors) and associated standard deviations are given in Table 4 for reference purposes.

Crystal-chemical discussion

Some interatomic distances and bond angles of interest are given in Table 5: the atomic sites are designated according to the sequence in which they are generated by the symmetry operations given for the general positions in the *International tables for x-ray crystallography*, Vol. I. The structure accommodates the Fe atoms, which are juxtaposed across the shared tetrahedral edges, by slight distortions from the ideal positions. The principal distortion is an increase in the

Table 5. *Some interatomic distances and bond angles of interest: standard deviations in parentheses*

Bond	Distance	Bond angle	Angle
Fe ₁ –S(1) ₁	2.213(7) Å	S(1) ₁ –Fe ₁ –S(2) ₁	111.0(4)°
Fe ₁ –S(2) ₁	2.307(6)	S(1) ₁ –Fe ₁ –S(2) ₅	110.7(3)
Fe ₁ –S(2) ₅	2.340(9)	S(1) ₁ –Fe ₁ –S(2) ₈	107.6(4)
Fe ₁ –S(2) ₈	2.200(6)	S(2) ₁ –Fe ₁ –S(2) ₅	105.3(3)
Fe ₁ –Fe ₅	2.818(7)	S(2) ₁ –Fe ₁ –S(2) ₈	110.2(2)
		S(2) ₅ –Fe ₁ –S(2) ₈	112.1(3)
Cu ₁ –S(1) ₁	2.251(8)		
Cu ₁ –S(2) ₁	2.332(9)	S(1) ₂ –Cu ₁ –S(2) ₁	108.4(3)
Cu ₁ –S(1) ₂	2.433(11)	S(1) ₂ –Cu ₁ –S(1) ₁	112.5(4)
		S(2) ₁ –Cu ₁ –S(2) ₇	102.7(5)
S(1) ₁ –S(2) ₁	3.725(9)	S(2) ₁ –Cu ₁ –S(1) ₁	112.2(3)
S(1) ₁ –S(2) ₅	3.748(10)		
S(1) ₁ –S(2) ₈	3.561(14)	Fe ₁ –S(1) ₁ –Fe ₇	110.1(5)
S(2) ₁ –S(2) ₅	3.696(13)	Fe ₁ –S(1) ₁ –Cu ₁	110.9(3)
S(2) ₁ –S(2) ₈	3.698(7)	Fe ₁ –S(1) ₁ –Cu ₂	107.8(3)
S(2) ₅ –S(2) ₈	3.767(10)	Cu ₁ –S(1) ₁ –Cu ₂	109.2(5)
S(1) ₁ –S(1) ₂	3.896(14)	Fe ₁ –S(2) ₁ –Cu ₁	112.2(4)
S(1) ₁ –S(2) ₁	3.805(9)	Fe ₁ –S(2) ₁ –Fe ₅	74.7(3)
S(2) ₁ –S(1) ₂	3.864(14)	Fe ₁ –S(2) ₁ –Fe ₈	113.0(3)
S(2) ₁ –S(2) ₇	3.641(20)	Cu ₁ –S(2) ₁ –Fe ₅	119.7(3)
		Cu ₁ –S(2) ₁ –Fe ₈	107.8(4)
		Fe ₅ –S(2) ₁ –Fe ₈	124.6(4)

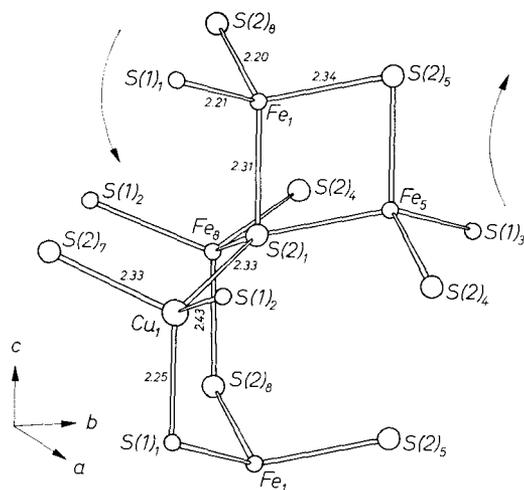


Fig. 2. The refined structure of cubanite enclosed within a sphere, 4.2 Å in radius, about S(2)₁

nearest Fe—Fe distance over the ideal distance (2.82 Å to 2.65 Å). This feature is also expressed in an increase in the lengths of bonds Fe₁—S(2)₅ and Fe₁—S(2)₁ (Fig. 2) relative to the Fe—S distance in chalcopyrite (below), and a decrease in the enclosed bond angle S(2)₁—Fe₁—S(2)₅ relative to the ideal-tetrahedral bond angle. In addition, the Fe, S coordination tetrahedra have been rotated, albeit somewhat irregularly, in the directions indicated. The distortion about the Cu atoms seems to be largely a consequence of that around the Fe atoms. In general, compared to the results of AZAROFF and BUEGGER, the present work suggests a greater distortion of the environments of the metal atoms.

Chalcopyrite, CuFeS₂, is a mineral with structural similarities to cubanite: the structure is based on close-packed S atoms with Cu and Fe coordinated in the four-fold interstices. The metal—S bond distances are Cu—S = 2.34 Å and Fe—S = 2.22 Å (PAULING and BROCKWAY, 1932), which are similar to the average bond distances in cubanite (2.34 Å and 2.27 Å respectively) and agree well with two of the four bonds about each metal (Fig. 2). Neutron-diffraction studies have shown that, in chalcopyrite, the Fe is present as Fe³⁺ in the high spin, *d*⁵ state, and the Cu as Cu⁺, *d*¹⁰ state (DONNAY *et al.*, 1958). The correlation of structural setting and bond lengths is good evidence for assuming similar electron configurations for these two metals in cubanite.

In respect to a metal—S bonding model for cubanite, then, the paired e electrons of the Cu atoms would be available to form π bonds and the six t_2 electrons would be antibonding (the former would tend to strengthen the σ bonds and the latter to weaken them), whereas, for the Fe atoms, the e electrons would be nonbonding and the three t_2 electrons antibonding. If we can correlate the bonding forces directly with interatomic distance, the effects of the extra three antibonding electrons on the Cu atoms seem greater than that of the π bonds. The σ bonds from the S(1) atoms are tetrahedrally disposed, so that they could be described as sp^3 tetrahedral hybrids. Of the σ bonds from S(2) atoms, three are tetrahedrally disposed but the fourth, to the juxtaposed Fe atom, is not; for example, the bond angle $\text{Fe}_1\text{—S}(2)_1\text{—Fe}_5$ is 74.7° . The redistribution of this bond has resulted in a pronounced stretching of the $\text{S}(2)_1\text{—S}(2)_5$ distance, 4.04 Å, compared to the average S—S distance of S atoms coordinated about Fe, 3.70 Å.

In addition to the effect of the nearest-neighbour metal—S bonding forces, it is necessary to consider the effect of the juxtaposed Fe atoms on each other and on the bonding in the crystal. NICKEL (1968) rationalized the structural stability of minerals with the pyrite, marcasite, arsenopyrite and löllingite structures on the basis of possible σ bonding between adjacent Fe atoms with singly occupied t_{2g} orbitals: the interatomic distances between Fe atoms spin-paired in this way are 2.85 Å for löllingite and 2.89 Å for arsenopyrite. However, BAIRD (1968) suggests that the nearest Fe—Fe distances in α Fe_2O_3 , 2.89 Å, indicate only a weak interaction (the Fe—Fe distance in α Fe is 2.482 Å) and it does seem that the Fe—Fe distances in löllingite and arsenopyrite are too great for full σ -bond formation. At the same time the evidence for a certain amount of t_{2g} orbital interaction (partial σ -bond formation) is quite compelling, and the argument could be extended to the cubanite structure. It could be argued that the singly occupied e orbitals of the Fe atoms are partially coupled across the shared tetrahedral edges, and it is the extra stability obtained from this which determines the final structure. The apparent stretching of the Fe—Fe distance is not intuitively in accord with this model, but, developing the conclusion of AZAROFF and BUERGER, it can be rationalized as repulsion between the adjacent, redistributed, Fe—S(2) σ -bonding orbitals. Conversely, it can be interpreted as indicating repulsive forces between the Fe atoms, which would suggest the alternative hypothesis that the e orbital along the inter-

atomic direction, say the d_{z^2} , is destabilized, resulting in spin pairing in the other ($d_{x^2-y^2}$) e orbital, and it is the π bonding contribution between this and the surrounding S atoms which stabilizes the configuration.

Weak ferromagnetism

The weak ferromagnetism of cubanite was ascribed by BUEGER (1945) to be a direct consequence of the structural peculiarity in which the Fe atoms are associated together in pairs across the shared tetrahedral edges. SAWADA *et al.* (1962) investigated the magnetic properties in some detail. The saturation magnetization was found to be 3.54 gauss (equivalent to 0.171 Bohr magnetons/unit cell). The magnetization was independent of temperature but disappeared abruptly on inversion to the cubic phase.

There are possible alternative causes for the weak ferromagnetism (uncompensated ferromagnetism and superparamagnetism), but the close association and probable interaction of the Fe atoms cannot be overlooked as the most likely one. According to DZYALOSHINSKY (1958) the weak ferromagnetism of α Fe₂O₃ is due to interaction of the electrons between iron atoms of two magnetic sublattices; the spins being canted from the ideal directions so that the two sublattice magnetic moments no longer cancel and a resultant moment remains. We would predict that, in cubanite, the paramagnetic Fe atoms would be arranged in two magnetic sublattices in such a way that in the "ideal" state the crystal would be antiferromagnetic. However, the close proximity of the Fe atoms would result in interaction of the electron spins to produce a resultant magnetic moment. The nearest Fe—Fe distance in cubanite is somewhat shorter than that in α Fe₂O₃, 2.89 Å. We can postulate that this indicates a greater degree of electron interaction and in part, at least, accounts for the greater spontaneous magnetization of cubanite.

Cubic modification of CuFe₂S₃

Single-crystal fragments of the Strathcona cubanite, 2–4 mm in length, were sealed under vacuum in 2 mm diameter silica-glass tubing. The charges were held at different temperatures for 14 days, and each was quenched in water at the termination of each run. The results are given in Table 6. The reaction was not reversed, so that we can state only that inversion temperature is 220 °C or less, essentially agreeing with the work of YUND and KULLERUD. However,

Table 6. *Thermal inversion of cubanite*

Run temperature	Product
298°C	Cubic
230°C	Cubic
220°C	Orthorhombic + cubic
209°C	Orthorhombic

the identification of the transformation product as cubic (and not tetragonal) was unambiguous, within the limits of resolution of the Jagodzinski camera; it is possible that the phase identified by YUND and KULLERUD as tetragonal was simply a mixture of cubanite and the cubic modification.

The lattice parameter of the cubic form determined from a standardized Jagodzinski film, is $a = 5.2949(3)$ Å, in good agreement with an earlier figure $a = 5.295$ Å (SAWADA *et al.*). The powder diffraction pattern was very similar to that of sphalerite: we note that d_{111} , 3.057 Å, closely correlates with d_{002} of cubanite, 3.117 Å, suggesting that [111] is a direction of closely-packed S atoms and that, structurally, the cubic form bears a similar relationship to cubanite as sphalerite does to wurtzite. A structural investigation of the cubic form was carried out on this basis. Intensity data were obtained from a Debye-Scherrer film of the cubic form synthesized by inversion at 298°C: the camera used had a diameter of 114.6 mm and the sample was held in the camera in a 0.2 mm diameter capillary tube. The data, normalized to 100.0 percent for the strongest reflection, compare very favourably (Table 7) with intensity data calculated assuming the sphalerite structure and random occupation of the cation sites, and positively identify the structural type. The calculated intensities are corrected for Lorentz and polarization effects and for absorption: the isotropic temperature factors were taken from

Table 7. *Comparison of the observed and calculated intensities for the cubic modification of CuFe₂S₃*

<i>hkl</i>	I_{obs}	I_{calc}	<i>hkl</i>	I_{obs}	I_{calc}
111	100.0	100.0	331	20.7	20.8
200	7.1	8.9	420	1.3	3.2
220	64.9	57.8	422	42.4	45.0
311	41.6	38.1	511	27.0	44.5
222	3.6	2.2	533		
400	10.5	10.5			

the cubanite refinement. The metal—S bond distance for this structure is 2.29 Å, very similar to the average metal—S distance in cubanite, 2.29 Å, although the calculated densities of the two structures are somewhat different, 4.048 g/cm³ for the cubic form, 4.021 g/cm³ for cubanite.

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References

- L. V. AZAROFF and M. J. BUEGER (1955), Refinement of the structure of cubanite, CuFe₂S₃. *Amer. Mineral.* **40**, 213–225.
- M. C. BAIRD (1968), Metal-metal bonds in transition metal compounds, in *Progress in inorganic chemistry*, F. A. COTTON (Ed.), Vol. **9**, Interscience Publishers, New York.
- M. J. BUEGER (1945), The structure of cubanite, CuFe₂S₃, and the coordination of ferromagnetic iron. *J. Amer. Chem. Soc.* **67**, 2056.
- M. J. BUEGER (1947), The crystal structure of cubanite, *Amer. Mineral.* **32**, 415–425.
- D. T. CROMER (1965), Anomalous dispersion corrections computed from self-consistent field relativistic Dirac-Slater wave functions. *Acta Crystallogr.* **18**, 17–23.
- D. T. CROMER and J. B. MANN (1968), X-ray scattering factors computed from numerical Hartree-Fock functions. *Acta Crystallogr. A* **24**, 321–323.
- G. DONNAY, L. M. CORLISS, J. D. H. DONNAY, N. ELLIOTT and J. M. HASTINGS (1958), Symmetry of magnetic structures: magnetic structure of chalcopyrite. *Physic. Rev.* **112**, 1917–1923.
- I. DZYALOSHINSKY (1958), A thermodynamic theory of “weak” ferromagnetism of antiferromagnetics. *J. Physics Chem. Solids* **4**, 241–255.
- M. E. FLEET (1968), On the lattice parameters and superstructures of pyrrhotites. *Amer. Mineral.* **53**, 1846–1855.
- W. C. HAMILTON (1965), Significance tests on the crystallographic *R* factor. *Acta Crystallogr.* **18**, 502–510.
- E. H. NICKEL (1968), Structural stability of minerals with the pyrite, marcasite, arsenopyrite and löllingite structures. *Can. Mineral.* **9**, 311–321.
- L. PAULING and L. O. BROCKWAY (1932), The crystal structure of chalcopyrite, CuFeS₂. *Z. Kristallogr.* **82**, 188–194.
- M. SAWADA, M. OZIMA and Y. FUJIKI (1962), Magnetic properties of cubanite (CuFe₂S₃). *J. Geomagn. Geoelect. Kyoko* **14**, 107–112.
- R. A. YUND and G. KULLERUD (1966), Thermal stability of assemblages in the Cu—Fe—S system. *J. Petrology* **7**, 454–488.