

## ON THE TRANSFORMATION OF CUBANITE \*

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### ABSTRACT

Orthorhombic cubanite transforms between 200° and 210°C directly to a face-centred cubic polymorph which is, in general, twinned along the (111) plane. The structural relationship between orthorhombic and cubic cubanite has been determined. The transformation appears to be irreversible in the laboratory, and annealing of cubic cubanite below the inversion temperature results in chalcopyrite exsolution. This is opposite to the relationship in which orthorhombic cubanite is frequently found as "exsolution" laths in a chalcopyrite matrix in mineral deposits.

### INTRODUCTION

Cubanite,  $\text{CuFe}_2\text{S}_8$ , usually occurs in ore deposits with chalcopyrite, and sometimes with talnakhite, pyrrhotite, and pentlandite. The crystal structure of cubanite (orthorhombic, space group  $Pcmm$ ,  $a = 6.467(1)$ ,  $b = 11.117(6)$ ,  $c = 6.231(2)\text{\AA}$ ,  $Z = 4$  (Szymanski 1973) has been studied previously by several investigators

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(e.g. Buerger 1945, 1947; Azaroff & Buerger 1955; Fleet 1970). The structure has been described by Buerger (1947) as being made up of slabs of the wurtzite structure parallel to (010) and  $b/2$  wide, joined to one another by inversion centres so that there is a sharing of an edge between adjacent iron co-ordination tetrahedra (Fig. 1). Wurtzite has a polar structure with all co-ordination tetrahedra pointing one way, but, in cubanite, half of the tetrahedra point one way and half the other. The mineral exhibits a weak ferromagnetic moment of 0.03 Bohr magnetons per Fe atom close to the  $b$ -axis direction and this is believed to result from the canting of the moments in two equivalent Fe sublattices of opposed spin (Fleet 1970; Townsend *et al.* 1972). Mössbauer studies of Imbert & Wintenberger (1968) have confirmed the existence of a magnetic coupling in cubanite; however, other Mössbauer work (Makarov *et al.* 1968) is difficult to comprehend because of possible confusion between orthorhombic and cubic cubanite.

There has been considerable work on the polymorphism of cubanite induced by heating. Pub-

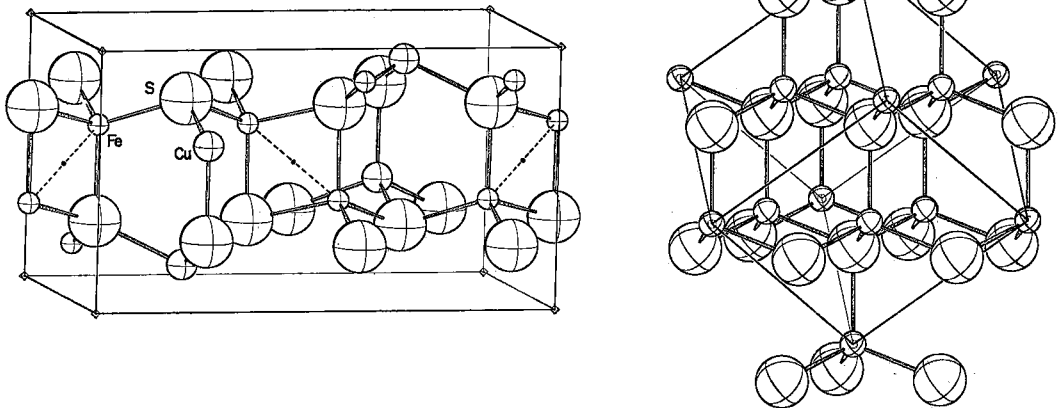


FIG. 1. Diagrammatic representation of orthorhombic cubanite (left) and of cubic cubanite (right) showing, respectively, the  $hcp$  and  $ccp$  arrangements of sulphur atoms, with their approximate relative orientation before and after transformation. For the orthorhombic cubanite cell, the  $a$  axis points towards the reader, the  $b$  axis is horizontal and the  $c$  axis is vertical. Dashed lines connect adjacent Fe atoms (2.804Å apart) via inversion centres. In cubic cubanite the small circles represent the disordered (Cu,Fe) sites, and the [111] direction of the sphalerite-like cell is vertical.

lications on this work include reports that cubanite transforms directly to a cubic phase either at 270°C (Sawada *et al.* 1962), at 220°C or lower (Fleet 1970), or between 200°C and 235°C (Mukaiyama & Izawa 1970). A direct transformation to a hexagonal phase has been suggested (Vaasjoki 1971). It has also been proposed that there is a tetragonal polymorph, intermediate between orthorhombic and cubic cubanite (Yund & Kullerud 1966), but this has not been substantiated further. Sawada *et al.* (1962) have reported that there is a decrease of saturation magnetization at room temperature to negligible values and that this transformation is accompanied by a disordering of Fe and Cu atoms. Fleet (1970) compared the observed and calculated intensities for high-temperature cubanite using powder diffraction data, and found good agreement assuming the sphalerite-like structure for the high-temperature form and random occupation of cations sites. He also noted the similarity between  $d_{111}$  of high-temperature cubanite and  $d_{002}$  of cubanite and from this suggested that the two forms bear a similar relationship to each other as does sphalerite to wurtzite.

#### Materials and techniques

A cubanite crystal (1.5 × 2 × 5 mm) from the Strathcona mine, Sudbury, Ontario, was sawn

\* Strictly speaking, this is intermediate solid solution (iss) of  $\text{CuFe}_9\text{S}_3$  composition (Cabri 1973) but we refer to it in this paper simply as cubic cubanite.

with a wire saw into five slices for use in the heating experiments (Table 1). These slices were subsequently characterized by reflection microscopy, by x-ray diffraction (Gandolfi, Debye-Scherrer, and precession cameras), and with an electron-probe microanalyser. Other cubanite crystals used from the same locality were too small and could be characterized only by x-ray diffraction. Annealing of specimens was done in horizontal furnaces (temperature controlled within 5°C), with the samples contained in sealed evacuated silica glass tubes. The annealing temperature was determined with a calibrated Pt-Pt/10% Rh thermocouple and the samples were quenched in ice-water.

#### EXPERIMENTAL RESULTS AND DISCUSSION

##### *The polymorphism of cubanite*

The heating experiments with the five slices are described in terms of the periods and temperature of annealing in Table 1 and the identification of the products is also detailed therein. X-ray diffraction powder patterns were taken for each of the specimens (#1-8) using a 57.3-mm Gandolfi camera and/or a 114.6 Debye-Scherrer camera with Fe-filtered  $\text{CoK}\alpha$  radiation. These patterns were compared with those of previously characterized cubic (high-temperature) cubanite\* (MacLean *et al.* 1972), chalcopyrite (Cabri & Hall 1972), and orthorhombic cubanite (Berry & Thompson 1962). In every case the measured patterns matched with one or more of the standards.

The results of the heating experiments on the sliced cubanite crystal (Table 1) show that ortho-

TABLE 1. HEATING EXPERIMENTS ON A CUBANITE CRYSTAL SLICED INTO FIVE SECTIONS

Specimen No.	Slice No.	Temp. °C	Time (days)	X-ray Identification	Polished Section and Microprobe Analysis
1	I	200	146	orthorhombic cubanite	-----
2	II	210	99	cubic cubanite > orthorhombic cubanite	Isotropic matrix except for 1 lamella (2x15µm)
3	III	300	7	cubic cubanite	One small area (2x5µm) deduced by microprobe to be pyrrhotite (area %=0.007%); rest of crystal is isotropic. Probe anal. identical to unheated cubanite.
4	III	100 (after 300 above)	24	cubic cubanite + minor chalcopyrite	Isotropic matrix (460x920µm) with 4 small areas of inclusions, all at the crystal edge. Largest inclusion is 12x12µm and all are two-phase (pyrite surrounded by pyrrhotite).
5	IV	224	7	cubic cubanite > orthorhombic cubanite	Isotropic matrix with few parallel areas of untransformed cubanite (Fig. 2). No compositional difference detected with microprobe.
6	IV	230 (after 224 above)	24	cubic cubanite	-----
7	IV	100 (after 230 above)	300	cubic cubanite + minor chalcopy. (same as #4)	Isotropic matrix of cubanite composition with one visible lamella of chalcopyrite approximately 2x10µm.
8	V	room temp.	--	orthorhombic cubanite	Single-phase $\text{CuFe}_2\text{S}_3$ .

rhombic cubanite transforms directly to a high-temperature cubic phase between 200 and 210°C and that the orthorhombic/cubic transformation is sluggish near the transition temperature. At no time was there any evidence of a hexagonal phase and this is discussed more fully below. Microscopic study of a polished section of specimen #5 (Fig. 2) shows that orthorhombic cubanite occurs as well-defined "domains" with respect to the cubic cubanite matrix. The distinct cracks perpendicular to *c* and less well-developed cracks parallel to *c* reported by Vaasjoki (1971) are also clearly visible in Figure 2.

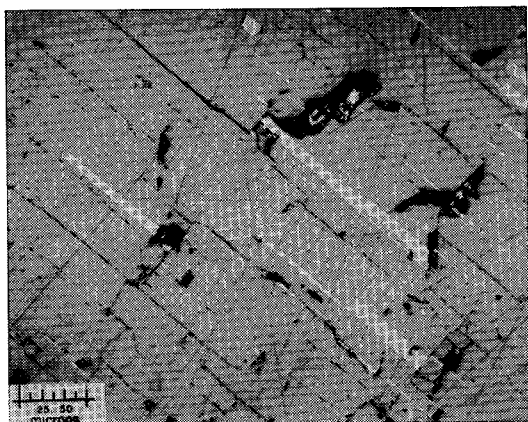


FIG. 2. Oriented "lamellae" of orthorhombic cubanite (lighter colour) in a matrix of high-temperature cubanite. The black, irregular areas are pits. Fractures parallel to the orthorhombic cubanite lamellae are clearly visible while the fine cross-cutting lines are scratches due to polishing. (Specimen #5, Table 1).

The existence of a reported "tetragonal" phase, intermediate between cubic and orthorhombic cubanite, was investigated in specimens #4 and #7. Table 2 lists the diffraction data for one of the specimens (#7), along with those of cubic cubanite ( $a = 5.283\text{\AA}$ ) and chalcopyrite ( $a = 5.28$ ,  $c = 10.40\text{\AA}$ ). The x-ray diffraction powder pattern does appear "tetragonal" as previously reported by Yund & Kullerud (1966) but a comparison of this pattern indicates that specimen #7 is simply a mixture of cubic cubanite and chalcopyrite. Since the cubanite pattern of specimen #8 (Table 1) is free of any extraneous lines, the chalcopyrite present in specimen #7 must have resulted on annealing. Corroborative evidence for the existence of this mixture was obtained by examining specimen #7 with an x-ray precession camera. A preliminary photographic survey with  $\text{MoK}\alpha$  radiation and expo-

sure times of 30 hours provided diffraction data that could be explained entirely in terms of a single crystal of cubic cubanite with  $a = 5.32\text{\AA}$ . This larger value is probably due to the different composition resulting from the exsolution of chalcopyrite. Longer exposure times ( $\sim 100$  hours) of the  $hk0$  and  $0kl$  films showed additional weak reflections which required an approximate doubling of the cubic cubanite cell dimensions in each direction. A detailed comparison of these data with that of chalcopyrite (Hall & Stewart 1973) showed that the weak reflections were in fact the 101, 301, 103, and 105 reflections of three chalcopyrite single crystals oriented with their axes parallel to the principal axes of cubic cubanite.

#### *Twinning at the orthorhombic/cubic transformation*

Experiments additional to those described in Table 1 were performed to determine the structural relationship between orthorhombic and cubic cubanite. Cubic cubanite crystals (annealed at 300°C and quenched) were examined using a precession camera and, with one exception, were found to be twinned. In every case where there was twinning, only two twin components, related by the twin plane normal to one of the  $[111]$  directions of the cubic structure, were observed. Diffraction intensities indicated that the proportions of these components were equal. This suggested that this  $(111)$  twin plane was unique and had a special relationship to the crystal lattice.

The relationship between the crystallographic axes of orthorhombic cubanite and the twinning direction in cubic cubanite was studied in the following manner. An irregular fragment of cubanite ( $\sim 0.4$  mm across) was determined to be a single crystal by means of x-ray precession photographs and was examined so that the orientation of the crystallographic axes was established in relation to the crystal form. This crystal was then transformed to the cubic polymorph and characterized with x-ray powder patterns using a Gandolfi camera. Further examination by the x-ray precession method showed it to have the twinning described above, with the twin plane of the cubic cell in the  $ab$  plane of the orthorhombic cell. The directional relationship of the orthorhombic (*o*) to cubic (*c*) cells is:  $[001]_o \parallel [111]_c$ ;  $[010]_o \parallel [101]_c$ ;  $[100]_o \parallel [121]_c$ .

The orthorhombic/cubic thermal transformation is noteworthy because it appears irreversible in the laboratory, and because orthorhombic cubanite has not been synthesized. The trans-

formation seems to be similar to that of wurtzite/sphalerite but, in orthorhombic cubanite, the hexagonal close-packed (*hcp*) sulphur matrix, with layers stacked *ABAB* parallel to the *ab* plane (*c*/2 apart), has half the metal atoms associated with these layers being above and half below (in slabs *b*/2 wide). The transformation to high-temperature cubanite must involve a movement of the metals to one particular side of the sulphur layers, accompanied by a disordering of

the metals and a reorganization of the sulphur layers to produce an *ABCABC* sequence of a sphalerite-like structure. The *hcp* to cubic close-packed (*ccp*) \* transformation in layer structures is not uncommon, particularly in metals and simple ionic compounds, and is based on stacking (twin) faults of these layers (Barrett 1952). If the polymorphic transformation nucleates at more than one point within the crystal, the initial layers of co-ordination tetrahedra may point in opposite directions (*i.e.*, the metals may be located on opposite sides of the *hcp* sulphur layers in different parts of the

\* A *ccp* arrangement of atoms results in a face-centred cubic (*fcc*) structure.

TABLE 2. X-RAY DIFFRACTION POWDER DATA

H.T. Cubanite <sup>1</sup>				Sample #7 <sup>2</sup>				Chalcopyrite <sup>3</sup>			
				H.T.cb.		cp.					
<i>hkl</i>	<i>I</i>	<i>d</i> <sub>meas</sub>	<i>d</i> <sub>calc</sub>	<i>I</i>	<i>d</i> <sub>meas</sub>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	<i>I</i>	<i>d</i> <sub>meas</sub>	<i>d</i> <sub>calc</sub>
111	10	3.049	3.050	10	3.052	3.052	3.034	101	2	4.71	4.711
				1	2.899		2.900	112	10	3.03	3.035
200	3	2.640	2.641	4	2.641	2.643	2.640	103	1	2.89	2.899
				$\frac{3}{2}$	2.602		2.603	200	3	2.64	2.642
220	8	1.867	1.868	$<\frac{3}{2}$	2.303		2.303	004	1	2.60	2.601
				8	1.871	1.867	1.867	211	1	2.30	2.304
311	7	1.594	1.593	3	1.854		1.854	220	4	1.867	1.868
				7	1.594	1.594	1.590	204	8	1.852	1.853
222	1	1.524	1.525	2	1.573		1.573	312	6	1.590	1.591
400	4	1.321	1.321	1B	1.527	1.526	1.517	116	3	1.572	1.573
				4	1.323	1.321	1.320	224	1	1.517	1.517
331	5	1.212	1.212	$\frac{3}{2}$	1.302		1.301	400	3	1.321	1.321
				5	1.215	1.213	1.210	008	1	1.302	1.301
420	1	1.180	1.181	2	1.204		1.203	332	2	1.210	1.211
422	6	1.078	1.078	$<\frac{3}{2}$	1.182	1.182		316	3	1.203	1.203
				6B	1.081	1.079	1.075	424	5	1.075	1.076
333	5	1.017	1.017	1	1.069		1.068	228	2	1.067	1.067
				5B	1.019	1.017					
440	3	0.935	0.934	1B	1.013		1.016	512	2B	1.017	1.016
				$\frac{3}{2}$ B	1.004		1.003	336	1B	1.012	1.011
				4B	0.935	0.934	0.933	1.1.10	1B	1.003	1.002
				1B	0.928		0.927	440	1	0.935	0.934
								408	3	0.928	0.928

1. Cubanite (cb) from Strathcona mine, Ont., heated to 300°C and quenched (MacLean *et al.* 1972). Pattern obtained with 57.3 mm Gandolfi camera.  $a=5.283(2)\text{Å}$ .

2. This study (114.6 mm Debye-Scherrer. For H.T. cb.  $a=5.286(1)$ ; for cp.  $a=5.28(1)$ ,  $a=10.41(1)\text{Å}$ .

3. Chalcopyrite (cp) from Western mines, B.C. (Cabri & Hall 1972).  $a=5.28(1)$ ,  $a=10.40(1)\text{Å}$ .

B = Broad line

crystal) and this will give rise to a twinned cubic lattice. The more nucleation points there are within a crystal, the greater is the probability of finding equal proportions of twins in the transformed lattice. If the proportion of twin components is equal, the symmetry of the twin-composite reciprocal lattice is  $6/mmm$ . This results in a pseudo-hexagonal lattice, with  $a(\text{hex}) = a(\text{cub})/\sqrt{2}$  and  $c(\text{hex}) = a(\text{cub}) \times \sqrt{3}$ . This probably accounts for the report by Vaasjoki (1971) that high-temperature cubanite is hexagonal with  $c = 9.17\text{\AA}$ . The structural changes required by this transformation may also explain why single crystals of untwinned cubic cubanite are small. Our experience has shown that, of the many cubic cubanite crystals examined, only the smallest ( $\sim 0.05$  mm) was found to be single with no twin component. Intensity data have been collected for this crystal and a detailed structure analysis is in progress. *The exsolution of chalcopyrite from*

#### *high-temperature cubanite*

The presence of single-crystal domains of chalcopyrite in specimen #7, oriented along the principal axes of cubic cubanite, seems to be consistent with the localized ordering of Cu and Fe atoms with decreasing kinetic energy. Under such conditions the metal atoms, starting at random nucleation points, may be located in specific interstices in the face-centred cubic sulphur matrix, in an order that is dictated by the anti-ferromagnetic and/or ionic covalent interactions. The single-crystal domains of chalcopyrite expand from these points until inhibited by discontinuities or fractures in the sulphur matrix, or by the unavailability of an equal proportion of Cu and Fe atoms at the chalcopyrite-cubic cubanite interface. The availability of an equal proportion of metal atoms depends, in large part, on the ability of these atoms to diffuse through the sulphur matrix at the time of chalcopyrite formation. Two factors, namely, temperature and the rate of cooling, are probably critical in the mobility of metal atoms in such a solid-state diffusion transformation. Such a formation process would account for the small amounts of chalcopyrite present in specimens #4 and #7. Indeed, chalcopyrite was observed only as a single lath ( $2 \times 10 \mu\text{m}$ ) in specimen #7 but could not be observed in specimen #4 which had been annealed for a shorter period of time, though it was detected by  $x$ -ray diffraction.

In mineral deposits, cubanite often occurs as laths in a chalcopyrite matrix, which is the reverse of the situation discussed above. The former textural relationship suggests a subsolidus process whereby exsolution of cubic cubanite

occurs in the host chalcopyrite, followed subsequently by the transformation of the cubic cubanite to the orthorhombic structure. The reverse relationship observed in our experiments in which chalcopyrite laths exsolve out of cubic cubanite matrix, with no apparent subsequent transformation to the orthorhombic cell, may be of importance to students of ore deposits. The irreversibility of the orthorhombic/cubic transformation in the laboratory may be due to different physico-chemical conditions existing in nature. On the other hand, the possibility that naturally occurring orthorhombic cubanite exsolved directly from a chalcopyrite matrix, or formed by other reactions below the transition temperature, cannot be excluded.

#### CONCLUSIONS

Cubanite transforms between 200 and 210°C directly to a face-centred cubic polymorph of  $\text{CuFe}_2\text{S}_3$  composition. This cubic cubanite is often twinned along the (111) plane which is the  $ab$  plane of orthorhombic cubanite. The mechanism of the transformation, though not fully understood, is thought to be similar to that of the wurtzite/sphalerite transformation.

Annealing experiments on cubic cubanite below the transformation temperature results in the exsolution of chalcopyrite laths from the cubic cubanite matrix. This relationship is the reverse of that commonly found in some ore deposits, where orthorhombic cubanite laths occur in a chalcopyrite matrix. This suggests that, in nature, orthorhombic cubanite may crystallize from a chalcopyrite matrix below 200-210°C.

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