Disorder of metal atoms in the structure of quenched high-temperature cubanite, CuFe_2S_3 , $Z=4/3$

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Abstract

Disorder of the metal atoms in the cubic cubanite, CuFe_2S_3 , $Z=4/3$, obtained by heating orthorhombic cubanite from Ohmine Mine at 300°C for 2 hours and quenched, is investigated by X-rays at room temperature. The cubic cubanite has the sphalerite-type structure with disordered arrangement of the Cu and Fe atoms in the tetrahedral interstices of sulfur atoms of cubic closest packing. The residual electron density around the metal sites in the difference synthesis indicates displacement of some of the metal atoms from the centers of the tetrahedra or anharmonic thermal motion in the tetrahedral sites. For a statistical split atom model, some (~6%) of metal atoms are displaced toward the four centers of sulfur triangles. The least-squares refinement of anharmonic thermal motion gives the third-order parameter of $c_{123}=0.00027(21)$.

Introduction

Cubanite CuFe_2S_3 has been one of the interesting minerals to mineralogists and physicists because of important ore mineral in Cu, Fe deposits and its weak ferromagnetism. Natural cubanite has orthorhombic symmetry and is known to invert to high-temperature form of cubic symmetry at above about 220°C. The transition is irreversible in the laboratory. The irreversibility is considered to be one of the reasons why synthesis of orthorhombic cubanite has not been successful yet even at considerably slow rate of cooling in the laboratory.

Since the first determination of the crystal structure of the orthorhombic form (Buerger, 1945), many structural investigations have been made to elucidate the physical property based on the refinements of the structure (Buerger, 1947; Azaroff and Buerger, 1955; Fleet, 1970; Szymanski, 1974a). The structure of the orthorhombic form is based on the hexagonal close-packed sulfur atoms with the ordered distribution of Cu and Fe atoms in tetrahedral interstices of sulfur atoms. The structure is related to the wurtzite structure.

The structure of the high-temperature form was confirmed to be the sphalerite-type (Fig. 1) based on the cubic close packed sulfur atoms with random

FIG. 1. The structure of cubic cubanite. S and M represent sulfur and metal atoms, respectively. V is "inverse" tetrahedral site in the sphalerite-type structure, which is not occupied by metal atoms.

occupation of Cu and Fe atoms in the tetrahedral sites of sulfur atoms (Fleet, 1970). Partial occupancy ($\sim 9\%$) of the metal atoms in the vacant tetrahedral sites in the sphalerite-type structure was determined by the single crystal method, indicating two possible interpretations, disordered distribution in the same cell or forming domains (Szymanski, 1974b). When the quenched high-temperature form was heated from room temperature to 350°C , slight anomaly of thermal expansion was observed at temperature range between 260° and 290°C (Mizota, 1977). The thermal expansion curve along the a -axis of cubic cubanite is shown in Fig. 2. The cell edge expands gradually with temperature rise, but it rather contracts from 260°C and again expands above 290°C . The thermal expansion data with the anomaly were confirmed with both heating and cooling experiments by means of the high-temperature X-ray powder diffractometer *in vacuo*. To elucidate the irreversibility of transition and abnormal expansion of cell dimension from the view point of crystallography, the further study of behaviour of the Cu and Fe atoms in the structure of the cubic form is stimulated as well as that of the orthorhombic form. In the present work, disorder of metal atoms in the cubic form is investigated at room temperature.

Experimental

Specimens of the cubic form of cubanite were obtained by heating orthorhombic cubanite from Ohmine Mine, Iwate, Japan, in an evacuated silica tube at 300°C for 2 hours and quenched in water. The specimens of orthorhombic cubanite were observed completely inverted to the cubic form by X-rays. For

FIG. 2. Thermal expansion curve along the a -axis of cubic cubanite obtained by means of a high temperature X-ray powder diffractometer (after Mizota, 1977). The expansion is slightly abnormal between 260° and 290°C. Half-solid triangles indicate the data obtained from heating process and solid inverse triangles from cooling process.

intensity data collection of Bragg reflections, the specimens were ground to sphere with an equipment devised by Mizota (1972). Attempts to obtain single crystals were unsuccessful because all the specimens investigated by X-rays showed spinel twin composed of twin individuals in two orientations. Both twin individuals have a (111) plane of the cubic form in common which is one of the close-packed planes of sulfur atoms (Cabri *et al.*, 1973). A spherical crystal of 0.18 ± 0.02 mm in diameter, with spinel twin, was used for data collection.

The unit cell constant was determined by Guinier camera method to be $a = 5.2972(5)$ Å, using $\text{CrK}\alpha$ radiation (2.2896 Å) with internal standard of silicon ($a = 5.43107$ Å).

The three-dimensional intensity data were collected on a Rigaku four-circle automated diffractometer. $\text{MoK}\alpha$ radiation (0.71069 Å) monochromatized with pyrolytic graphite was used. The data collection was carried out at room temperature. Within the range of $2\theta = 90^\circ$, intensities of 387 reflections of two octants were measured for one twin individual. Some reflections from each twin individual were superimposed and excluded from averaging intensity of equivalent reflections. According to geometrical relations between both reciprocal lattices of spinel twin, at least, one independent reflection of each twin individual is not superimposed in the intensity data measured (Fig. 3). This means it is not always necessary to use a single crystal for collecting intensity data if absorption correction can be made. Independent 50 reflections were obtained by averaging intensity of equivalent reflections. Lorentz and polarization corrections were applied. Spherical absorption correction was made with linear absorption coefficient of 127.2 cm^{-1} for $\text{MoK}\alpha$ radiation.

FIG. 3. Relationships of reciprocal lattices in two different orientations, (a) and (b), for spinel twin. The reflections 111 of both twin individuals are superimposed, but the reflections $1\bar{1}\bar{1}$, are not.

Structure refinement

The space group $F\bar{4}3m$ of the sphalerite-type was assumed for cubic cubanite in the structure investigation. The structure analysis was started from the sphalerite-type structure in which sulfur atoms are arranged in cubic closest packing. The Cu and Fe atoms were assumed to be distributed at random in four of the eight tetrahedral interstices of sulfur atoms ($4c$; $1/4, 1/4, 1/4$) in the unit cell. Therefore, the chemical constituents in the unit cell is $(\text{CuFe}_{2/4/3})\text{S}_4$. The least-squares refinement varying one scale factor and individual temperature factors for metal and sulfur atoms, was carried out and the final R value dropped to 0.064. During the refinements unit weight was given to all reflections. Scattering factors for non-ionized atoms were taken from International Tables for X-ray Crystallography (1962). The mean scattering factor of $(f_{\text{Cu}} + 2f_{\text{Fe}})/3$ for the metal atom was used for the calculation of the structure factor. Positional parameters and final isotropic temperature factors are given in Table 1. The comparison of the observed and calculated structure factors is given in Table 2. After the refinements, the Fourier and difference syntheses were calculated (Fig. 4). Residual electron density which is tetrahedrally distributed according to the symmetry of the space group $F\bar{4}3m$ was observed around the sites of metal atoms in the difference synthesis. No residual was observed in the "inverse" tetrahedral site ($4d$; $3/4, 3/4, 3/4$) in the Fourier and difference syntheses.

TABLE 1. Atomic parameters and isotropic temperature factors of high-cubanite CuFe_2S_3 .

atom	site	x	y	z	B
S	4a	0	0	0	1.45(10) $\text{\AA}^2$
M*	4c	1/4	1/4	1/4	1.57(6)

* M represents the metal atom of $(\text{Cu}+2\text{Fe})/3$.

FIG. 4. The Fourier (a) and difference (b) syntheses of cubic cubanite at room temperature. Only around the tetrahedral sites are shown in (b). S, M and V represent the same as in Fig. 1. T represents a center of sulfur triangle. Contours are arbitrary in (a), and at intervals of $0.6 \text{ e}\text{\AA}^{-3}$ with the lowest contour at $|0.6| \text{ e}\text{\AA}^{-3}$; positive contours are represented as full lines and negative contours are dotted, the zero line being omitted in (b).

To elucidate the residual electron density around the metal atoms, two models, that is, a split atom model and anharmonic thermal motion model, were introduced. For the split atom model, least-squares refinements were diverged because of strong correlations among positional parameters of split metal atoms. Therefore trial and error method was employed. The best result was obtained based on comparison of the observed and calculated structure factors, in which model some ($\sim 6\%$) of the metal atoms are displaced toward four triangular faces of sulfur tetrahedron. The R value slightly dropped from 0.064 of non-split atom model to 0.061 of split atom model. The refinements for thermal motion of third-order anharmonicity of the metal atoms were also carried out. The

TABLE 2. Observed and calculated structure factors of high-cubanite CuFe_2S_3 at room temperature.

h	k	l	$ F_o $	$ F_c $
1	1	1	104.3	98.8
0	0	2	35.3	38.1
0	2	2	102.6	102.4
2	2	2	28.7	27.7
1	1	3	72.4	67.0
1	3	3	50.2	50.4
3	3	3	46.1	39.5
0	0	4	66.6	75.3
0	2	4	18.6	19.1
0	4	4	45.8	47.3
2	2	4	60.5	58.9
2	4	4	10.1	9.8
4	4	4	32.0	32.1
1	1	5	37.8	39.5
1	3	5	31.4	31.8
1	5	5	21.8	21.6
3	3	5	25.1	26.1
3	5	5	20.3	18.1
5	5	5	12.6	13.0
0	0	6	9.7	9.8
0	2	6	33.5	38.7
0	4	6	5.1	6.0
0	6	6	20.6	19.1
2	2	6	7.9	7.5
2	4	6	27.1	26.8
2	6	6	2.6	3.7
4	4	6	4.1	4.3
4	6	6	14.7	14.0
6	6	6	2.1	2.4
1	1	7	18.6	21.6
1	3	7	18.2	18.1
1	5	7	13.2	13.0
1	7	7	8.0	8.2
3	3	7	14.8	15.3
3	5	7	11.6	11.1
3	7	7	8.5	7.1
5	5	7	9.7	8.2
0	0	8	19.1	22.6
0	2	8	4.6	4.3
0	4	8	15.8	16.3
0	6	8	0.5	2.6
2	2	8	17.3	19.1
2	4	8	2.0	3.3
2	6	8	11.9	10.3
4	4	8	13.2	12.0
1	1	9	10.9	11.1
1	3	9	8.6	9.6
1	5	9	7.5	7.1
3	3	9	9.7	8.2
0	0	10	1.7	2.6

metal site has point symmetry $\bar{4}3m$ and a variable third-order parameter of c_{123} . The least-squares refinements were converged and $c_{123}=0.00027(21)$ was obtained with the same R value for the isotropic refinement.

All the computations in the present work were carried out at the Computation Center of Osaka University and at the Institute for Protein Research of Osaka University, using the UNICS System (Sakurai, 1967) and RFINE (Finger, 1972).

Description and discussion

The structure of cubic cubanite is basically a sphalerite-type in which the Cu and Fe atoms are distributed in disorder in the tetrahedral interstices of sulfur atoms of cubic closest packing as previously described (Fleet, 1970; Szymanski, 1974b). The lattice constant ($5.2972(5)$ Å) obtained in this work is in good agreement with values reported in the literatures (Sawada *et al.*, 1962; Fleet, 1970; Cabri *et al.*, 1973; Szymanski, 1974b).

In the difference syntheses, the distribution of the residual positive peaks is tetrahedrally arranged around the metal sites. Two interpretations are possible for the features. One is a split atom model, that is, metal atoms are distributed in disorder in greater than or equal to two sites in the tetrahedral interstices. The other is anharmonic thermal vibrations of the metal atoms in the tetrahedral sites.

In the split atom model, some of the metal atoms, probably Cu atoms, or all atoms, are displaced from the center of tetrahedron toward one of the triangles of sulfur atoms. The displacement results in nearly triangular coordination which is often observed for Cu atoms in sulfides (e.g. anilite Cu_7S_4 , Koto and Morimoto, 1970; chalcocite Cu_2S , Evans, 1971). If we assume both Cu and Fe atoms behave the same anharmonic thermal motion in cubic cubanite, it is possible to refine based on such anharmonic model. In this work, however, it is rather difficult to determine which is correct of the two possibilities, the split atom model or the anharmonic thermal motion model, based on the results of refinements.

According to the refinements of cubic cubanite by Szymanski (1974b), the metal atoms are disordered and mainly distributed in the metal sites (4c) of the sphalerite-type structure, but about one-tenth of the metal atoms are located in the "inverse" tetrahedral sites of sulfur tetrahedron, which are not occupied by metal atoms in the sphalerite structure. In this work no positive residual electron density was observed in the "inverse" tetrahedral site in the Fourier and difference syntheses (Fig. 4). The difference of the two results might be attributed

to the difference of heating and annealing process of each cubic cubanite.

Recently, abnormal increase of heat capacity (C_p) of quenched cubic cubanite was observed in the temperature range 200–300°C using an adiabatic calorimeter (Mizota *et al.*, 1982). This anomaly indicates a possible presence of a higher order phase transition. Quenched β -PbF₂ has high ionic conductivity above the second-order phase transition at about 430°C (Derrington *et al.*, 1976), though it has the antiferite-type structure below and above the transition temperature. Anion behaviour of β -PbF₂ was studied in relation to conduction mechanism of ions at elevated temperatures (Koto *et al.*, 1980). The results of β -PbF₂ suggest easier atomic diffusiveness of cubic cubanite above the transition temperature and stimulate the structure investigation at elevated temperatures. Takeno *et al.* (1973) measured the electric conductivity of orthorhombic cubanite from Sudbury, heated cubic cubanite and synthetic cubic cubanite up to above the transition temperature. The electric conductivity curve of synthetic cubanite shows abnormal raise of the conductivity above room temperature. Whereas, this is not observed for the heated cubic cubanite but rather constant value up to above the transition temperature. They described the electric property of cubic cubanite is metallic with the conductivity of order of 10 ohm⁻¹ cm⁻¹. Such high conductivity may prevent to detect the trace of the ionic part of the conductivity of cubic cubanite if present.

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