Canadian Mineralogist
Vol. 23, pp. 77-82 (1985)

THE HEAT CAPACITY OF CUBANITE AND THE ANOMALY IN CUBIC $CuFe_2S_3$

TADATO MIZOTA
Department of Mining and Mineral Engineering, Faculty of Engineering, Yamaguchi University, Ube 755, Japan

HIROFUMI TANAKA
Shin-Kamaishi Mining Co., Kamaishi 026-02, Japan

YUJIRO FUJII
Department of Mining and Mineral Engineering, Faculty of Engineering, Yamaguchi University, Ube 755, Japan

KICHIRO KOTO
Institute of Scientific and Industrial Research, Osaka University, Mihoga-oka, Ibaraki, Osaka 565, Japan

ABSTRACT

Heat capacities of cubanite (orthorhombic $CuFe_2S_3$) and of its cubic polymorph have been measured from room temperature to 315°C by means of an adiabatic calorimeter. The enthalpy of transformation of cubanite to cubic $CuFe_2S_3$ has been determined to be 16.6 kJ/mol. The transformation is irreversible and so sluggish that the latent heat is observed over a wide range of temperatures between about 220 and 280°C. The quenched cubic form shows an anomaly in the heat-capacity curve between 170 and 300°C. This anomaly is endothermic on heating and corresponds to 1.20 kJ/mol ($CuFe_2S_3$) excess enthalpy. Repeated measurements of heat capacities give reproducible data. This indicates the possible existence of a kind of glass transition due to the randomized positions of metal atoms in the undercooled cubic form.

Keywords: cubanite, cubic $CuFe_2S_3$, heat capacity, transition enthalpy, glass transition in a sulfide.

SOMMAIRE

On a mesuré la capacité calorifique de la cubanite ($CuFe_2S_3$ orthorhombique) et de son polymorphe cubique de la température ambiante à 315°C au moyen d'un calorimètre adiabatique. Nous avons déterminé l'enthalpie de la transformation orthorhombique - cubique; elle est de 16.6 kJ/mole. C'est une transformation irréversible et si lente que la chaleur latente se manifeste dans un domaine étendu de température, de 200 à 280°C, environ. La forme cubique trempée montre une anomalie dans sa capacité calorifique entre 170 et 300°C. Cette anomalie, endothermique à la chauffe, correspond à 1.20 kJ/mole ($CuFe_2S_3$) d'enthalpie en excès. Des mesures répétées de la capacité calorifique reproduisent la valeur initiale. Ceci indiquerait l'existence d'une transition analogue à celle d'un verre, due au désordre de position des atomes de métal dans la forme cubique trempée.

(Traduit par la Rédaction)

Mots-clés: cubanite, cubic $CuFe_2S_3$, capacité calorifique, enthalpie de transition, transition de verre dans un sulfure.

INTRODUCTION

Cubanite, orthorhombic $CuFe_2S_3$, is known to transform sluggishly to a high-temperature cubic modification above 220°C (Fleet 1970, Szymański 1974, Putnis 1977). As the transformation is irreversible, no one has succeeded so far in the synthesis of the low-temperature form, although it has relatively simple chemical composition and crystal structure and is one of the important phases in the system Cu–Fe–S.

A quantitative evaluation of the heat of transformation from orthorhombic to cubic forms of $CuFe_2S_3$ in the temperature range 250–300°C was reported to be 5.6 kcal/mol (23.4 kJ/mol) by differential thermal analysis (DTA) (Dutrizac 1976). Recently, Ikeda *et al.* (1983) determined the heat of transformation to be 16.4 kJ/mol by a differential scanning calorimetry (DSC).

Adiabatic calorimetry is superior to DTA or similar methods for the quantitative measurement of heat values. The method, however, generally requires more sample, so that it is difficult to apply the technique to minerals that are not easy to prepare in a pure state. Recently, an adiabatic calorimeter that requires only a small amount of sample was fabricated for the investigation of minerals (Mizota *et al.* 1983). This calorimeter has a sample container of 2.6 cm^3 and can be used for measurements from room temperature to 800°C. The temperature has been calibrated with Sn and Bi metals within the accuracy of ±0.25 K. The heat-capacity values obtained using certified α-Al_2O_3 were found to be accurate within ±1-2 % of the data given by Ditmars & Douglas (1971).

The equipment mentioned above was used to measure the heat capacities of the orthorhombic and the cubic forms of $CuFe_2S_3$ from room temperature to 315°C, to elucidate the behavior of the irreversible phase-transformation in cubanite.

EXPERIMENTAL

Sample preparation and purity

Cubanite from the Ohmine mine, Iwate, Japan, was ground to -145 + 200 mesh. To eliminate impurities, composed mainly of chalcopyrite and hornblende, the powder was purified by means of an isodynamic separator and by a panning method using water. Because of the intimate intergrowth with fine-grained chalcopyrite and contamination with silicates, it was difficult to prepare pure cubanite. The sample contained a negligible amount of other sulfide minerals such as pyrrhotite and pyrite, as seen under the ore microscope. It was difficult to evaluate precisely the amount of the chalcopyrite contaminant in a small quantity by ore microscopy or X-ray powder diffraction. The sample was analyzed chemically for Cu, Fe, S and an acid-insoluble fraction to characterize the cubanite sample (Table 1). To obtain a precise chemical composition, especially required for an estimate of the small amount of chalcopyrite, a gravimetric analysis combined with the atomic absorption method was necessary. For example, Cu content was determined by electrogravimetry, and the residual copper (less than 0.2 % lost by the electrowinning) was checked and recovered by the atomic absorption analysis. The total obtained, 98.65%, indicates the presence of other elements that could not be determined in the analysis. We also analyzed chalcopyrite from the Washi-aimori mine, which occurs as fine euhedral crystals and is considered pure (Mukaiyama *et al.* 1968), by the same method to certify the reliability of analyses.

The analytical results on chalcopyrite are considered to be sufficiently accurate to calculate the percentage of cubanite in the sample. Assuming end-member compositions for cubanite and chalcopyrite, the composition of the sample is 92.38% cubanite, 3.03 % chalcopyrite, 4.59 % hornblende and unknowns. The adsorbed water is neglected in this calculation, because the sample was dried before the calorimetric measurement.

TABLE 1. CHEMICAL COMPOSITIONS OF THE SAMPLE

	Cubanite from the Ohmine mine			Chalcopyrite from the Washi-aimori mine		
Component	wt.%	mole ratio		wt.%	mole ratio	
Cu	22.45	1.011	3.00	34.00	0.989	2.00
Fe	38.84	1.989		30.55	1.011	
S	33.29	2.995		34.52	1.990	
Res.	3.57			0.26		
H_2O-	0.50					
Total	98.65			99.38		
Ideal formula		$CuFe_2S_3$			$CuFeS_2$	

Res.: Acid insoluble residue by ignition, mainly hornblende

Measurement of heat capacity

The heat capacity Cp of cubanite was measured twice in an atmosphere of nitrogen gas at about 0.5 atm, using about 3 g of sample for each experiment. To eliminate contamination by oxygen, the nitrogen gas was introduced into the calorimeter through a column filled with pure copper-metal turnings heated to 400°C. The heat capacity of cubanite was measured from room temperature to 315°C, above the temperature of transformation to the cubic form (Table 2). The sample was then cooled to room temperature in the calorimeter. As the transformation is irreversible, the cubic form can be supercooled to room temperature. The heat capacity of the cubic form was measured twice from room temperature to 315°C with the same sample.

TABLE 2. SPECIFIC HEAT CAPACITY OF CUBANITE

T /°C	Cp /$JK^{-1}g^{-1}$ 1	Cp /$JK^{-1}g^{-1}$ 2
30	0.5202	0.5371
40	0.5373	0.5410
50	0.5446	0.5509
60	0.5462	0.5546
70	0.5491	0.5582
80	0.5556	0.5580
90	0.5579	0.5654
100	0.5615	0.5662
110	0.5638	0.5714
120	0.5710	0.5737
130	0.5699	0.5742
140	0.5739	0.5846
150	0.5835	0.5882
160	0.5855	0.5985
170	0.5896	0.5975
180	0.5892	0.5970
190	0.5876	0.5987
200	0.5949	0.5957
210	0.5980	0.6093
220	0.6064	0.6191
230	0.6369	0.6359
240	0.7900	0.7278
250	5.0039	2.9009
260	1.9897	3.9038
270	0.6829	0.8596
280	0.6758	0.6784
290	0.6541	0.6705
300	0.6398	0.6520
310	0.6400	0.6531

Sample wt.	Elec. power supplied
1: 3.00892 g	310 mW
2: 2.88526 g	450 mW
	at room temp.

The cycle of measurements was repeated twice for two different samples. Therefore, the heat capacity of the cubic form was measured four times from room temperature to 315°C (Table 3). Leakage of heat was corrected from two measurements at different rates of heating by using the empty calorimeter (Mizota *et al.* 1983). Sample amount and experimental conditions are shown in Tables 2 and 3. Electric power supplied and temperature of the sample were measured at intervals of 30 seconds. A set of data in each ten-degree interval was used for the least-squares calculation to obtain the average values at 10 K intervals.

Measurement of the enthalpy of transformation

Samples of 1.15–1.23 g of cubanite were used to measure the enthalpy of transformation. Before each measurement, the sample was heated in advance in the calorimeter at 200°C for 1 hour to eliminate water. The measurements were carried out three times at different values of electric power supplied to the calorimeter for the correction of heat leakage arising from the different rates of heating. The experimental conditions are shown in Table 4.

TABLE 3. SPECIFIC HEAT CAPACITY OF CUBIC FORM OF $CuFe_2S_3$

T /°C	Cp /$JK^{-1}g^{-1}$ Sample 1 (1)	Sample 1 (2)	Sample 2 (1)	Sample 2 (2)	Average (σ)*
30	0.5613	0.5666	0.5679	0.5551	0.563(6)
40	0.5758	0.5766	0.5747	0.5706	0.574(3)
50	0.5760	0.5810	0.5810	0.5791	0.579(2)
60	0.5859	0.5827	0.5824	0.5792	0.583(3)
70	0.5916	0.5927	0.5961	0.5955	0.594(2)
80	0.5964	0.5975	0.6016	0.6029	0.600(3)
90	0.6036	0.6025	0.6011	0.5981	0.601(2)
100	0.6050	0.6067	0.6100	0.6067	0.607(2)
110	0.6049	0.6071	0.6019	0.5995	0.603(3)
120	0.6067	0.6092	0.6133	0.6038	0.608(4)
130	0.6023	0.6050	0.6011	0.6076	0.604(3)
140	0.6050	0.6058	0.6137	0.6084	0.608(4)
150	0.6091	0.6117	0.6130	0.6124	0.612(2)
160	0.6148	0.6158	0.6226	0.6168	0.618(3)
170	0.6188	0.6211	0.6228	0.6183	0.620(2)
180	0.6219	0.6260	0.6208	0.6261	0.624(3)
190	0.6306	0.6315	0.6374	0.6327	0.633(3)
200	0.6386	0.6422	0.6469	0.6378	0.641(4)
210	0.6485	0.6497	0.6530	0.6439	0.649(4)
220	0.6633	0.6608	0.6628	0.6585	0.661(2)
230	0.6743	0.6751	0.6753	0.6662	0.673(4)
240	0.6805	0.6894	0.6879	0.6846	0.686(4)
250	0.6876	0.6936	0.6981	0.6964	0.694(5)
260	0.6944	0.7017	0.7061	0.7037	0.701(3)
270	0.6926	0.7001	0.7080	0.7024	0.701(6)
280	0.6877	0.6958	0.7027	0.7011	0.697(7)
290	0.6639	0.6722	0.6866	0.6807	0.676(10)
300	0.6389	0.6470	0.6607	0.6564	0.651(10)
310	0.6402	0.6484		0.6622	0.650(11)
320		0.6500			

* The standard deviation (σ) is shown at the last digit(s) of each value in parentheses.
Electric power supplied for sample 1 and 2 at 200°C was 310 and 450 mW, respectively. Sample wt. 1: 3.00892 g, 2: 2.88526 g

RESULTS

Heat capacity of cubanite

In Figure 1, heat capacities of cubanite obtained from two measurements with different rates of heating are shown by circles. The open and solid circles show values of electric power of 450 and 310 mW, respectively, supplied at room temperature. The heat capacity increases gradually to 200°C; above that temperature, an intense transformation-peak occurs and continues to about 275°C. The curve obtained from the slow rate of heating is the same as that from the rapid one except for the sharpening of the peak, which comes from the sluggishness of the transformation (Fig. 1, Table 1). An anomaly in the heat capacity of the cubic form is observed as a small node on each heat-capacity curve over 270°C.

Transformation enthalpy of the orthorhombic to the cubic form of $CuFe_2S_3$

Figure 2 shows the temperature *versus* time plots for three measurements of the enthalpy change. Except for the period of transformation, these plots before and after the transformation can be approximated by two straight lines. The transformation duration Δt is defined by the separation between these straight lines at the middle of the transformation temperature, as shown in each heating curve in Figure 2. The electric power supplied multiplied by Δt gives the transformation enthalpy Δ*H*, which is shown in Table 4 together with some experimental data for each experiment. To correct for heat leakage in the calorimeter, the three points in Δ*H versus* Δt plot of Figure 3 are extrapolated along the regression line to the ordinate at Δt = 0. The extrapolated

TABLE 4. DATA REQUIRED FOR THE MEASUREMENT OF THE TRANSFORMATION ENTHALPY ΔH

Run No.	wt. g	P mW	Ts mV	Te mV	Δt s/g	ΔH J/g
1	1.15060	131.30	9.81	10.30	419.3	55.06
2	1.23730	75.850	9.68	10.10	705.6	53.52
3	1.23020	48.125	9.56	9.99	1088.1	52.37

P: Average electric power supplied during transformation;
Ts and Te: temperatures at start and end of the transformation as electromotive force of CA-thermocouple; Δt: transformation duration

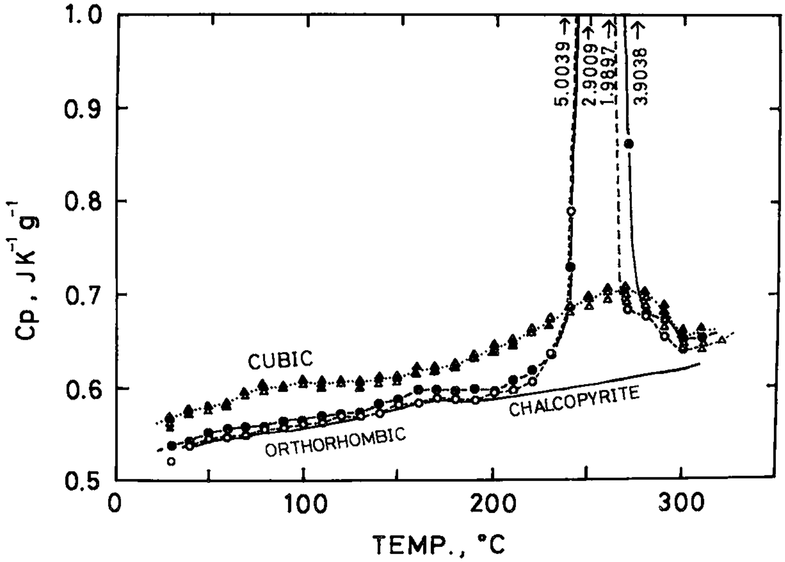

FIG. 1. Heat capacities of cubanite and the cubic form of $CuFe_2S_3$. Two measurements of cubanite are shown by open and solid circles, corresponding to values of electric power supplied of 310 and 450 mW, respectively. Values of the transformation peak that are off scale at 250 and 260°C are written in numerically. Four measurements of the cubic form from two samples are shown by triangles, many of which are superposed with the other plots. Heat capacity of chalcopyrite (Mizota *et al.* 1983) is shown as a solid line.

value, 56.58 J/g, is considered to be the transformation enthalpy corrected for the heat leakage of the apparatus. Furthermore, the value must be revised owing to the contamination, calculated from Table 1, by silicate (4.59%, mostly hornblende) and chalcopyrite (3.03%), which exhibit no transformation in this temperature range: 56.58/(1–0.0762) J/g = 61.25 J/g = 16.62 kJ/mol ($CuFe_2S_3$).

Heat capacity of cubic $CuFe_2S_3$

Specific heat-capacities of the quenched cubic form are given in Table 3 and are plotted in Figure 1 (denoted as triangles). The four results are in good agreement within the accuracy of the calorimeter. The average values of the specific heat-capacities and the associated standard deviation σ are shown in the last column of the table. The most interesting feature is that the curve shows an elevation in specific heat between about 170 and 300°C. After correction for contained impurities, this anomaly corresponds to 1.20 kJ/mol and 1.88 $JK^{-1}mol^{-1}(CuFe_2S_3)$ of excess enthalpy and entropy, respectively, if the normal specific heat is supposed to be a straight line connecting two values at 170 and 300°C.

DISCUSSION

The orthorhombic-to-cubic transformation enthalpy of cubanite from the Ohmine mine determined in this work is smaller than the value of 5.6 kcal/mol (23.4 kJ/mol) for cubanite from the Frood–Stobie mine, Sudbury, determined by the DTA method (Dutrizac 1976). Those data included an error of 25% in the worst case. The precision of measurement of the enthalpy, 16.6 kJ/mol ($CuFe_2S_3$) in this work, is within ±1%. The difference between both is over 29% and should be considered significant. Cubanite from Sudbury shows sharp X-ray-diffraction spots in comparison with those from the Ohmine mine. This indicates that the former has a better crystallinity than the latter. This may be one of the reasons for the smaller transformation-enthalpy for the Ohmine cubanite. We have no idea at present, however, on how the degree of crystallinity, which includes the magnetic order, affects the value of the transformation enthalpy. The present data are in good agreement with the 16.4 kJ/mol value determined by Ikeda *et al.* (1983), who examined cubanite from the Komori mine, Kyoto, Japan, by the DSC method. They calculated the enthalpy theoretically considering four components, *i.e.*, the disordering of the metals ΔH_d, magnetic moment ΔH_m, lattice reconstruction and magnetic fluctuation Δ. As the last term is hard to evaluate at present and the lattice-reconstruction term is considered to be small and negligible, they proposed: $\Delta H = \Delta H_d + \Delta H_m - \Delta = 8.2 + 12.3 -$

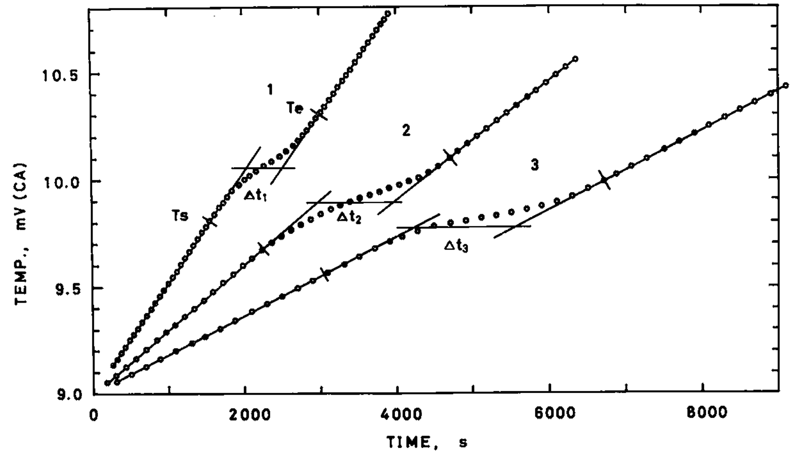

FIG. 2. Time–temperature plots to determine the transformation enthalpy of cubanite. On each plot, two regression lines, before and after the transformation, are drawn. The transformation period is shown between the two lines, in which Ts and Te represent the starting and final temperatures, respectively. At the middle point between Ts and Te, two regression lines determine the duration of the transformation Δt.

Δ kJ/mol. This shows that the ΔH should be smaller than 20.5 kJ/mol.

The anomaly in the heat capacity found in the cubic form is an interesting phenomenon. Mizota *et al.* (1983) measured the heat capacity of chalcopyrite from the Washi-aimori mine by means of the calorimeter from 30 to 310°C. The chemical composition of this specimen is shown in Table 1. The heat-capacity curve (Fig. 1) shows no anomaly between 170 and 300°C. Examining the heat-capacity curve of orthorhombic $CuFe_2S_3$ around 200°C and considering the fact that the silicate impurity is composed mostly of hornblende, we conclude that the anomaly is attributable to the cubic $CuFe_2S_3$. The crystal structure of chalcopyrite is similar to that of the cubic form of $CuFe_2S_3$, as both structures are fundamentally of the sphalerite type. The absolute value of the specific heat-capacity of chalcopyrite is very close to that of cubanite to 200°C. In other words, the heat capacity of the cubic $CuFe_2S_3$ is unusually high over the whole range of temperature investigated. Both chalcopyrite and cubanite have a small peak at about 160°C in their specific-heat curves (Fig. 1), but these peaks are too small to be considered significant.

Putnis (1977) pointed out that "On cooling the disordered cubic structure, cation ordering takes place as an alternative to the transformation back to hexagonal close-packing, but in the absence of an ordering scheme at this composition based on the cubic subcell, the ordering process results in the exsolution of chalcopyrite." In this work, the anomaly in the heat capacity is observed in each experiment, and the possible structural change accompanied by this anomaly is considered to be not as sluggish as the exsolution because the heating rate in this experiment is almost 1.5 K/min. No new exsolution-texture was observed in cubic $CuFe_2S_3$ heated at 300°C for 1 hour in the present experiment. The exsolution reaction in cubic $CuFe_2S_3$ does not occur or occurs very slowly at low temperatures between 200 and 300°C (Sugaki & Yamae 1952, Cabri *et al.* 1973). Therefore, the anomaly must be attributed to some reversible structural changes in the cubic form, such as order–disorder of cations or formation of a domain structure. Mizota & Koto (1983) investigated the cation distribution in the quenched cubic form by X-ray diffraction at room temperature and proposed a displacement model of partially occupied metal

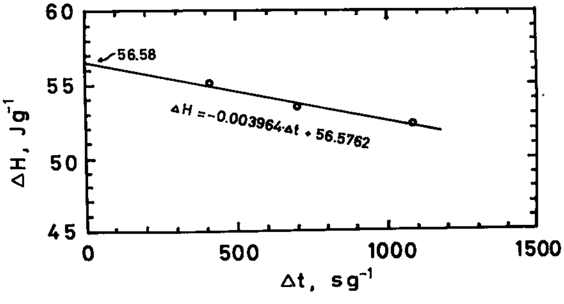

FIG. 3. Plot of Δt *versus* ΔH for the cubanite transformation, intended to correct for the leakage of heat from the calorimeter. The formula of the regression line is shown. The corrected ΔH is 56.58 J/g (sample).

positions from the centre of the sulfur tetrahedron or anharmonic thermal motion in the tetrahedral site. The heat-capacity anomaly of cubic $CuFe_2S_3$ suggests that the statistically distributed metal atoms at low temperature become mobile in the lattice above 170°C. This mechanism might be a reasonable explanation for such a small anomaly in the heat capacity. This anomaly may indicate a preliminary step in the decomposition described by Putnis (1977).

The transformation found in cubic $CuFe_2S_3$ is similar to the glass transition of crystalline materials (Suga & Seki 1974), because on cooling below 300°C, the diffusive movement of metal is considered frozen. When the cubic form is heated, relaxation of the frozen atoms of metal occurs between 170 and 300°C. This must explain the heat-capacity anomaly, but the explanation needs to be followed up by further investigations.

The significance of this transformation comes from the fact that the basic structure of cubic $CuFe_2S_3$ is the same as that of the intermediate solid-solution *iss* in the system Cu–Fe–S. There have been many investigations of *iss*, mainly at temperatures over 300°C (Merwin & Lombard 1937, Hiller & Probsthain 1956, Yund & Kullerud 1966, Genkin *et al.* 1966, Cabri 1973). The transformation, however, will have an influence below 300°C.

ACKNOWLEDGEMENTS

The authors express their sincere thanks to Professor H. Suga of Osaka University, for his valuable discussions and critical reading of the manuscript. We are also grateful to the referees for their comments and critical reviews. Thanks are also due to Professor R.F. Martin and Dr. J.T. Szymański for their kind advice, which greatly improved this paper.

REFERENCES

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

______, HALL, S.R., SZYMAŃSKI, J.T. & STEWART, J.M. (1973): On the transformation of cubanite. *Can. Mineral.* **12**, 33-38.

DITMARS, D.A. & DOUGLAS, T.B. (1971): Measurement of the relative enthalpy of pure α-Al_2O_3 (NBS Heat capacity and enthalpy standard reference material No. 720) from 273 to 1173 K. *J. Res. Nat. Bur. Standards A. Phys. Chem.* **75A**, 401-420.

DUTRIZAC, J.E. (1976): Reactions in cubanite and chalcopyrite. *Can. Mineral.* **14**, 172-181.

FLEET, M.E. (1970): Refinement of the crystal structure of cubanite and polymorphism of $CuFe_2S_3$. *Z. Krist.* **132**, 276-287.

GENKIN, A.D., FILIMONOVA, A.A., SHADLUN, T.N., SOBOLEVA, S.V. & TRONEVA, N.V. (1966): On cubic cubanite and cubic chalcopyrite. *Geol. Rudn. Mestorozhd.* **8**(1), 41-54 (in Russ.).

HILLER, J.-E. & PROBSTHAIN, K. (1956): Thermische und röntgenographische Untersuchungen am Kupferkies. *Z. Krist.* **108**, 108-129.

IKEDA, M., ISHII, T., MIYAMOTO, Y. & KUME, S. (1983): Phase change of cubanite studied with diamond anvil cell. *J. Mineral. Soc. Japan* **16**, *Special issue* 1, 191-198.

MERWIN, H.E. & LOMBARD, R.H. (1937): The system Cu–Fe–S. *Econ. Geol.* **32**, 203-284.

MIZOTA, T. & KOTO, K. (1983): Disorder of metal atoms in the structure of quenched high-temperature cubanite, $CuFe_2S_3$, $Z = 4/3$. *Mineral. J.* **11**, 213-221.

______, TANAKA, H., FUJII, Y. & SHIMA, H. (1983): An adiabatic calorimeter for the calorimetric measurement of minerals. *J. Mineral. Soc. Japan* **16**, *Special issue* 1, 39-47.

MUKAIYAMA, H., IZAWA, E. & NAKAE, Y. (1968): The chemical composition and the structure of natural chalcopyrite. *J. Mineral. Soc. Japan* **9**, 81-91.

PUTNIS, A. (1977): Electron microscope study of phase transformations in cubanite. *Phys. Chem. Minerals* **1**, 335-349.

SUGA, H. & SEKI, S. (1974): Thermodynamic investigation on glassy states of pure simple compounds. *J. Non-Cryst. Solids* **16**, 171-194.

SUGAKI, A. & YAMAE, N. (1952): Thermal study on the intergrowth of chalcopyrite and sphalerite. *Sci. Rep. Tokoku Univ., Ser. III*, **4**, 103-110.

SZYMAŃSKI, J.T. (1974): The crystal structure of high-temperature $CuFe_2S_3$. *Z. Krist.* **140**, 240-248.

YUND, R.A. & KULLERUD, G. (1966): Thermal stability of assemblages in the Cu–Fe–S system. *J. Petrology* **7**, 454-488.

Received February 22, 1984, revised manuscript accepted May 10, 1984.