HIGH-TEMPERATURE ENTHALPIES AND ENTROPIES OF CHALCOPYRITE AND BORNITE

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CONTENTS

ILLUSTRATIONS

TABLES

HIGH-TEMPERATURE ENTHALPIES AND ENTROPIES OF CHALCOPYRITE AND BORNITE

by

L. B. Pankratz[1] and E. G. King[2]

ABSTRACT

Enthalpies were determined for synthetic chalcopyrite ($CuFeS_2$) between 298° and 1,050° K and for synthetic bornite (Cu_5FeS_4) between 298° and 1,100° K by copper-block drop calorimetry. Two transitions were found for each compound. The lower transitions were both crystal transformations from tetragonal (low-temperature form) to cubic (high-temperature form). The chalcopyrite transformation occurred at 830° K with a heat of transformation of 2,405 cal/mole; the bornite transformation was at 485° K with a heat of 1,430 cal/mole. The other transitions were of the second order and were presumed to be magnetic in character. The second-order transitions for chalcopyrite occurred at 930° K, and the one for bornite at 540° K.

Enthalpy increments, entropy increments, and heat capacities are tabulated at even temperatures above 298.15° K. Equations of enthalpy are also given.

INTRODUCTION

Quantitative data on thermodynamic properties are of great importance in developing new metallurgical processes or improving existing techniques. Such basic data then have a real value in the effective utilization of mineral resources. From this standpoint the absence in the literature of thermodynamic data for the important copper minerals, chalcopyrite and bornite, is surprising.

As part of a Bureau of Mines copper and base metals program, this report gives the results of enthalpy determinations above 298° K for these substances. Chalcopyrite was investigated to 1,050° K and bornite to 1,100° K. The corresponding entropy increments and heat capacity values have been derived and tabulated.

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Later thermochemical investigations will provide standard enthalpies and entropies of formation for both chalcopyrite and bornite.

MATERIALS

Both compounds were synthesized by the same method, which utilized high-purity copper, iron, and sulfur as starting materials. Copper and iron were first separately dissolved in HNO_3. The solutions were then dehydrated, and the residues were ignited to the oxides. The iron oxide was partially reduced by H_2 and then mixed with stoichiometric amounts of the CuO. After these mixtures were almost completely reduced with H_2, they were ground and mixed again before being completely reduced. This procedure assured an intimate mixture of powders having fine particle sizes. Silica-glass bulbs were filled with the Cu-Fe mix, and sulfur was added in stoichiometric amounts. It was necessary to place the bulbs in an ice bath when adding the sulfur, as some reaction occurred even at room temperature. After filling, the bulbs were placed in steel bombs; they were then heated at 300° C overnight, and finally at 650°-685° C for 3 days. Upon cooling, the bulbs were opened and the samples were ground and mixed in a nitrogen atmosphere before being chemically analyzed. Any needed adjustments in composition were made, and the bulbs were reloaded, resealed, and heated again according to the same procedure. In this manner two adjustments in composition were made for chalcopyrite and one for bornite. Chemical analyses of the final products are given in table 1. Spectrographic analyses showed silicon in both samples, in amounts less than 0.01 percent. Other impurities detected by this means were present in negligible quantities. X-ray diffraction patterns of the samples matched those in the ASTM Catalog of X-Ray Powder Data. Both compounds were tetragonal in crystal structure at room temperature.

TABLE 1. - Chemical analyses, weight-percent

Component	Chalcopyrite ($CuFeS_2$)		Bornite (Cu_5FeS_4)	
	Actual	Theoretical	Actual	Theoretical
Copper......	34.60	34.62	63.27	63.31
Iron........	30.38	30.43	11.14	11.13
Sulfur......	34.98	34.95	25.54	25.56
Total..	99.96	100.00	99.95	100.00

MEASUREMENTS AND RESULTS

The copper-block calorimeter described by Douglas and King (2)[3] was used for the enthalpy determinations. Results are expressed in defined calories (1 cal = 4.1840 joules). The International Practical Temperature Scale of 1968 was used throughout. Molecular weights were calculated from the 1967 Table of Atomic Weights (3). Sample masses were chalcopyrite, 6.8838 g; and bornite, 7.9805 g. Silica-glass capsules, for which enthalpies were determined in separate experiments, were used to contain the samples for the enthalpy determinations.

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Table 2 lists the experimental values. Figures 1 and 2 show the enthalpies plotted as the function $(H_T-H_{298.15})/(T-298.15)$ against temperature. The standard error is 0.08 percent for chalcopyrite and 0.15 percent for bornite. The absolute uncertainty is estimated to be 0.3 percent. Determinations for chalcopyrite were terminated when the capsule exploded because of sulfur vapor pressure while being heated at 1,100° K. The investigation of bornite was temperature limited by the measuring apparatus. The last reported enthalpy for bornite was at 1,105° K.

TABLE 2. - Experimental enthalpy values for chalcopyrite and bornite

T, ° K	$H_T-H_{298.15}$, cal/mole	T, ° K	$H_T-H_{298.15}$, cal/mole	T, ° K	$H_T-H_{298.15}$ cal/mole
CHALCOPYRITE					
400.4	2,475	745.7	11,920	901.5	19,680
401.3	2,500	753.2	12,130	903.0	19,705
451.3	3,785	775.4	12,860	925.5	21,040
475.2	4,415	802.8	13,770	935.0	21,555
505.3	5,220	820.3	14,510	944.9	21,995
509.1	5,310	830.4	17,025	960.4	22,580
552.2	6,475	840.3	17,375	980.7	23,435
602.8	7,855	850.4	17,745	1,004.6	24,430
650.9	9,200	859.5	18,025	1,024.8	25,305
702.2	10,630	871.3	18,460	1,050.3	26,300
BORNITE					
398.9	6,130	532.2	17,350	701.5	30,970
431.7	8,210	539.7	18,180	750.0	34,720
452.3	9,545	540.7	18,235	799.6	38,635
460.3	10,180	550.1	18,985	849.6	42,445
469.9	11,065	550.4	19,040	899.7	46,315
478.3	12,440	552.4	19,185	953.0	50,515
485.1	13,130	561.2	19,920	1,004.6	54,575
510.6	15,375	570.7	20,665	1,048.7	58,150
510.6	15,380	601.2	23,070	1,105.3	62,765
519.9	16,255	604.9	23,335		
530.3	17,320	650.2	26,950		

A first-order transition was found for chalcopyrite at 830° K with an isothermal heat of transition of 2,405 cal/mole. A second-order transition (having zero isothermal heat) was determined at 930° K. Two transitions were also found for bornite--one of first order near 485° K with a heat of transition of 1,430 cal/mole, and one of second order near 540° K.

Chalcopyrite and bornite prepared as described in a previous section (at approximately 675° C) showed rapidly reversible behavior during the enthalpy

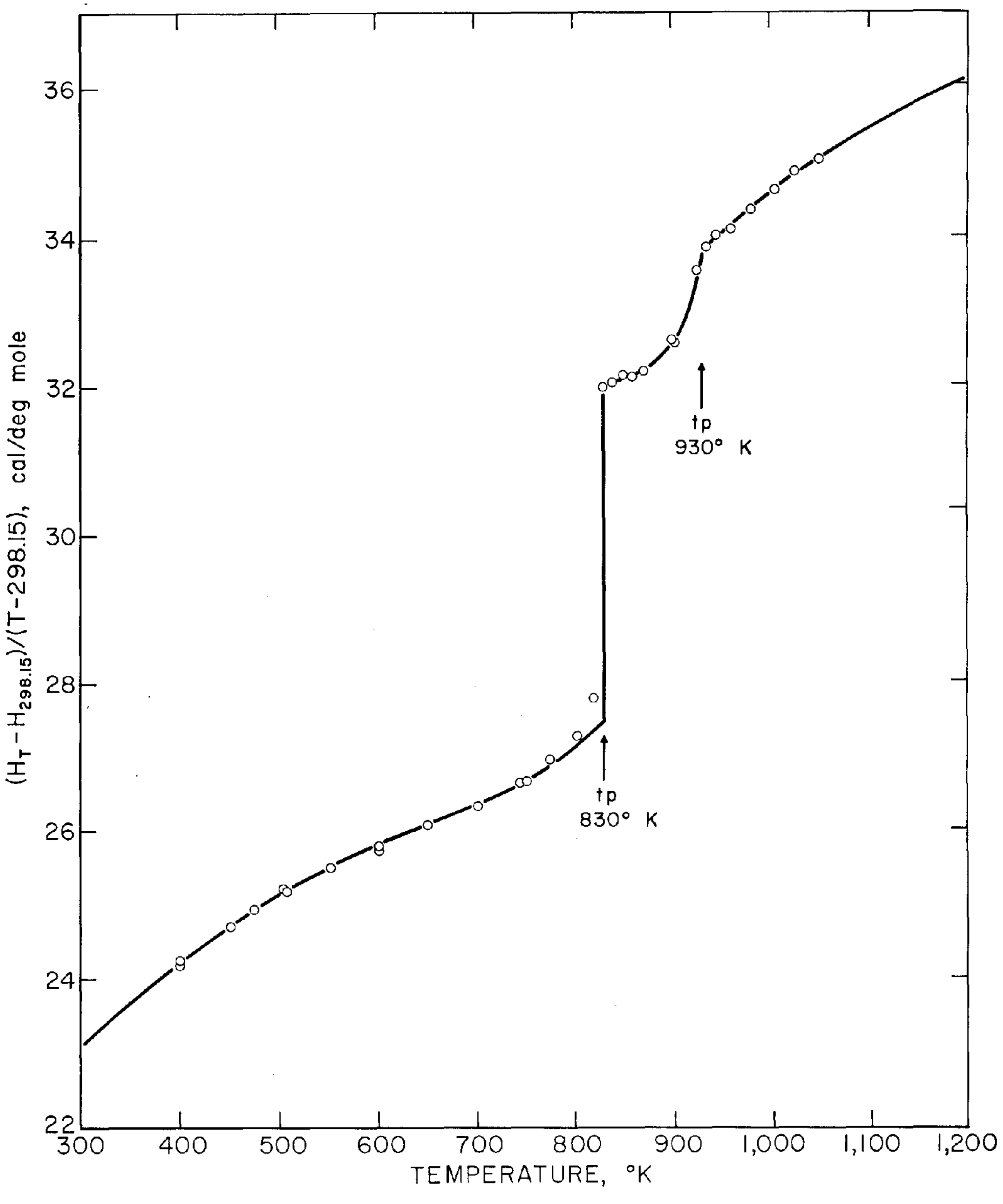

FIGURE 1. - Enthalpy Functions of Chalcopyrite ($CuFeS_2$).

determinations. To test for phase reversibility, separate samples were cooled from high temperatures to 298° K in the same manner as was done during the enthalpy determinations, and then within minutes subjected to X-ray

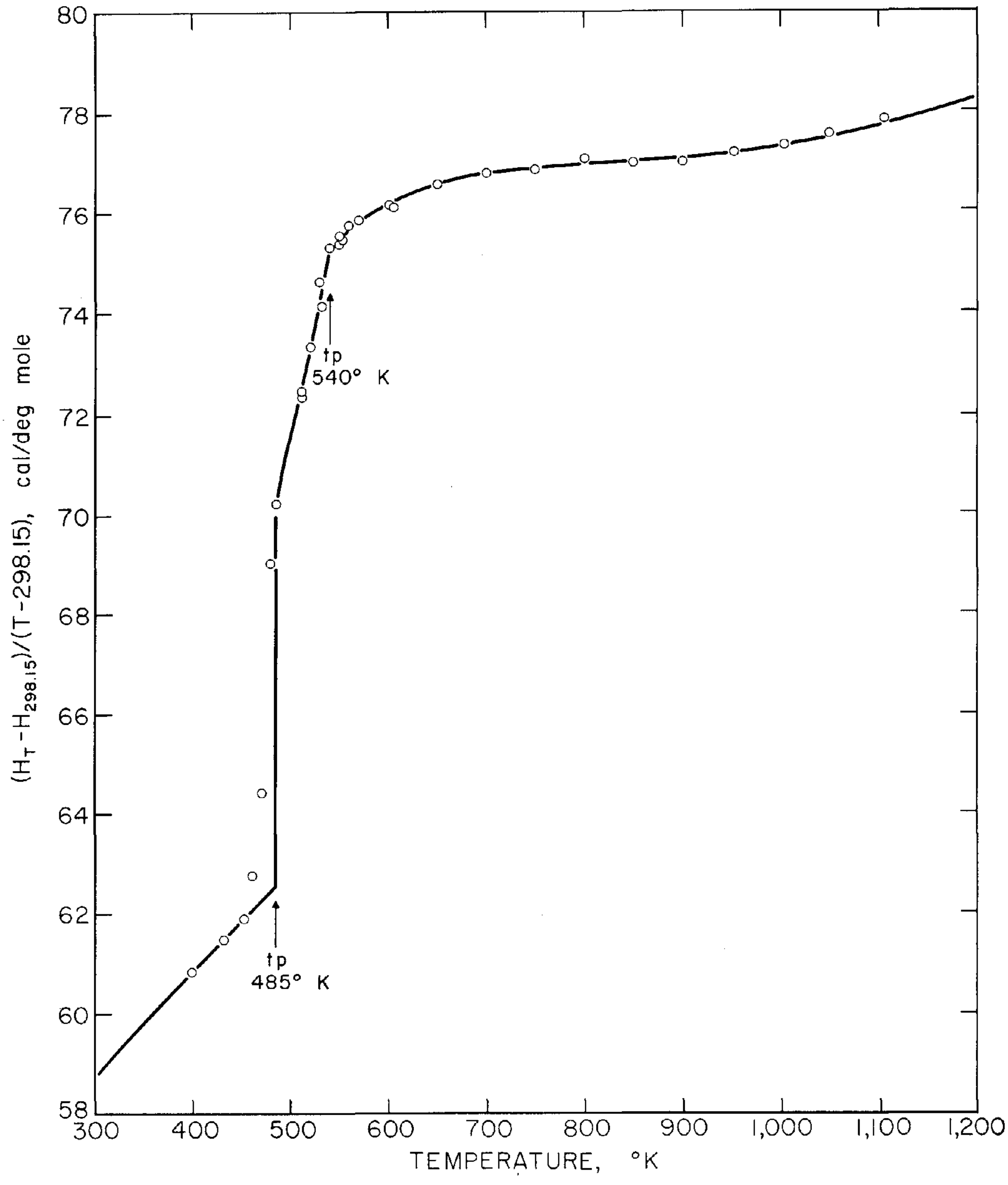

FIGURE 2. - Enthalpy Functions of Bornite (Cu_5FeS_4).

diffraction analysis. Two such analyses were made for chalcopyrite, at 897° and 993° K; three were made for bornite, at 510°, 550°, and 685° K. In all cases both compounds were shown to revert to their room-temperature tetragonal form.

Polynomial functions were fitted to the experimental enthalpy data by computer methods. These functions were used to calculate the enthalpy increments at even temperatures and to derive the heat capacities and entropy increments, all of which are given in tables 3 and 4.

TABLE 3. - Thermodynamic functions at even temperatures for chalcopyrite ($CuFeS_2$)

T, °K	C_p, cal/deg mole	$S_T-S_{298.15}$, cal/deg mole	$H_T-H_{298.15}$, cal/mole
298.15	22.89	0	0
350	24.26	3.79	1,225
400	25.29	7.10	2,465
450	26.10	10.12	3,750
500	26.69	12.91	5,070
550	27.11	15.47	6,420
600	27.46	17.85	7,780
650	27.89	20.06	9,165
700	28.64	22.15	10,575
750	30.05	24.17	12,040
800	32.56	26.18	13,600
830 (α)	34.83	27.42	14,610
830 (β)	36.21	30.32	17,015
850	34.29	31.15	17,715
900	46.21	33.29	19,590
930 (β)	75.07	35.22	21,355
930 (γ)	41.22	35.22	21,355
950	41.22	36.10	22,180
1,000	41.22	38.21	24,240
1,050	41.22	40.22	26,300
[1]1,100	(41.22)	(42.14)	(28,360)
[1]1,150	(41.22)	(43.97)	(30,425)
[1]1,200	(41.22)	(45.73)	(32,485)

[1] Values in parentheses are extrapolations.

TABLE 4. - Thermodynamic functions at even temperatures for bornite (Cu_5FeS_4)

T, °K	C_p, cal/deg mole	$S_T-S_{298.15}$, cal/deg mole	$H_T-H_{298.15}$, cal/mole
298.15	58.71	0	0
350	60.90	9.59	3,100
400	62.95	17.85	6,200
450	64.92	25.38	9,395
485 (α)	66.25	30.29	11,690
485 (β)	85.08	33.24	13,120
500	89.02	35.89	14,425
520	94.28	39.49	16,260
540 (β)	99.53	43.14	18,195
540 (γ)	80.52	43.14	18,195
600	79.31	51.56	22,985
700	77.98	63.68	30,845
800	77.52	74.05	38,610
900	77.91	83.19	46,375
1,000	79.17	91.46	54,225
1,100	81.29	99.10	62,240
[1]1,200	(84.27)	(106.29)	(70,510)

[1] Values in parentheses are extrapolations.

For those who prefer to use the data in algebraic form, the following equations were fitted by Kelley's method (4) to the enthalpies from tables 3 and 4. Both the average deviation of these equations from the tabular data and their temperature ranges of validity are given in parentheses.

Chalcopyrite

$$\alpha:\quad H_T-H_{298.15} = 20.79T + 6.40 \times 10^{-3}T^2 + 1.34 \times 10^5T^{-1} - 7{,}217$$

(0.4 percent; 298°-830° K).

$$\beta:\quad H_T-H_{298.15} = -141.40T + 105.00 \times 10^{-3}T^2 + 62{,}042$$

(0.3 percent; 830°-930° K).

$$\gamma:\quad H_T-H_{298.15} = 41.22T - 16{,}979$$

(0.1 percent; 930°-1,200° K).

Bornite

$$\alpha:\quad H_T - H_{298.15} = 49.76T + 17.54 \times 10^{-3}T^2 + 1.35 \times 10^5 T^{-1} - 16{,}848$$

(0.1 percent; 298°-485° K).

$$\beta:\quad H_T - H_{298.15} = -34.31T + 123.50 \times 10^{-3}T^2 + 710$$

(0.1 percent; 485°-540° K).

$$\gamma:\quad H_T - H_{298.15} = 80.33T - 1.02 \times 10^{-3}T^2 - 24{,}886$$

(0.2 percent; 540°-1,200° K).

DISCUSSION

Chalcopyrite

The phase transformation found here for chalcopyrite at 830° K was reported by Yund and Kullerud (7) to be a change from low-temperature tetragonal to high-temperature cubic structure. The temperature of inversion was reported by them to be 820° K, as determined by the DTA method. The rapid reversibility reported here for the transformation was also noted by Yund and Kullerud. These workers pointed out, however, that the presence of a small amount of the cubic form mixed with predominately tetragonal material cannot be ruled out, in view of the close similarity of the X-ray diffraction patterns.

The second transition, found at 930° K for chalcopyrite, was presumed to be of the second order. Donnay and coworkers (1) and Raj and coworkers (6) reported this mineral to be antiferromagnetic at room temperature, with iron in the ferric state and copper in the cuprous state. Donnay conducted neutron diffraction studies and Raj investigated Mössbauer spectra. The temperature of 930° K, then, was taken to be the Néel temperature with no change in phase involved. Yund and Kullerud (7) support this conclusion by claiming the stable form of chalcopyrite to be isometric at 970° K. It should be mentioned that the enthalpy data obtained here could be treated so as to consider this second transition to be of the first order. In this case the entropy increments in table 3 for temperatures above 830° K would be decreased slightly, but the enthalpy values reported below 830° K and above 930° K would remain unchanged. Magnetic susceptibility measurements could determine whether or not 930° K is in fact the antiferromagnetic transition temperature.

Bornite

Morimoto and Kullerud (5) examined the high-temperature crystal structure behavior of bornite. They found, by X-ray diffraction analysis of chilled samples, that a crystal transformation took place near 501° K. The present investigation has determined the temperature of transformation to be about 485° K. Slight compositional differences can be expected to cause some variation in the temperature of transition. This agreement, therefore, is satisfactory. By X-ray analysis at high temperatures, Morimoto and Kullerud determined the crystal change to be from tetragonal (low-temperature form) to cubic (high-temperature form). Upon rapidly quenching the high-temperature cubic form (a = 5.50A), they found that the compound rapidly changed to a second cubic form with a = 10.94A. The latter modification was found to be metastable and spontaneously changed to tetragonal over a few days.

In an earlier discussion we stated that, with our method of sample preparation and mode of cooling during the enthalpy determinations, the phase transition (high-temperature cubic to tetragonal) was found to be rapidly reversible for run temperatures above 485° K. However, lattice constant data as given by Morimoto and Kullerud for the tetragonal and cubic forms show that, as in the chalcopyrite case, the X-ray diffraction patterns would be quite similar. Therefore, the possibility exists here also that a minor amount of the cubic form could be present with the tetragonal in the calorimetrically cooled product.

A previously unreported second-order transition was found for bornite at 540° K. It may be inferred from the high-temperature X-ray work of Yund and Kullerud (7) that stoichiometric bornite retains the cubic form to 973° K. We, therefore, infer that the transition found at 540° K is a magnetic one.

SUMMARY

This investigation of high-temperature enthalpies has provided the first quantitative thermodynamic data for chalcopyrite and bornite. The research has confirmed two crystal transformations found by others and has reported on two other transitions not previously described in the literature.

REFERENCES

1. Donnay, G., L. M. Corliss, J. D. H. Donnay, N. Elliott, and J. M. Hastings. Symmetry of Magnetic Structures: Magnetic Structures of Chalcopyrite. Phys. Rev., v. 112, No. 6, 1958, pp. 1917-1923.

2. Douglas, T. B., and E. G. King. High-Temperature Drop Calorimetry. Ch. 8 in Experimental Thermodynamics, v. 1, Calorimetry of Non-Reacting Systems, ed. by J. P. McCullough and D. W. Scott. Butterworths, London, 1968, pp. 293-331.

3. International Union of Pure and Applied Chemistry, Division of Inorganic Chemistry, Commission on Atomic Weights. Atomic Weights of Elements 1967. Pure and Appl. Chem., v. 18, No. 4, 1969, pp. 571-579.

4. Kelley, K. K. Contributions to the Data on Theoretical Metallurgy. XIII. High-Temperature Heat Content, Heat-Capacity, and Entropy Data for the Elements and Inorganic Compounds. BuMines Bull. 584, 1960, 232 pp.

5. Morimoto, N., and G. Kullerud. Polymorphism in Bornite. Am. Miner., v. 46, 1961, pp. 1270-1282.

6. Raj, D., K. Chandra, and S. P. Puri. Mössbauer Studies of Chalcopyrite. J. Phys. Soc. Japan, v. 24, No. 1, 1968, pp. 39-41.

7. Yund, R. A., and G. Kullerud. Thermal Stability of Assemblages in the Cu-Fe-S System. J. Petrology, v. 7, No. 3, 1966, pp. 454-488.

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