

Electric and Magnetic Properties of Bornite, Cu_5FeS_4

—With a Review of the Physical Properties of Cu-Fe-S Minerals—

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with 3 Tables and 7 Text-figures

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ABSTRACT:

The electric and magnetic properties of synthetic and natural bornites are considered to be in an intimate relation to transformation of their crystal structures.

It has become evident that the electric conductivity reveals increment in its value with increasing temperature and anomalous changes at 180°C and 300°C where transformation from the low-temperature tetragonal form to the transitional intermediate one and that from the intermediate to the high-temperature cubic one are assumable to appear, the substance under consideration is a typical semiconductor with activation energy of 0.25~0.35 eV in case of the low form and 0.54 eV in case of the high form, the magnetic susceptibility decreases paramagnetically with increasing temperature and shows anomalies at the temperature mentioned above and applying Curie-Weiss law to the susceptibility versus temperature curves below 180°C, it is possible to obtain $6.68\mu_B$ as the effective Bohr magneton number and -664°K for the asymptotic Curie temperature, respectively.

The electric and magnetic properties have been discussed in connection with those of Cu-Fe-S minerals such as FeS_x , FeS_2 , CuS, Cu_2S , CuFeS_2 , and CuFe_2S_3 .

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I. INTRODUCTION

Bornite, a common and widespread mineral occurring in plenty of the important copper deposits in considerable amounts, is believed to have been formed under various geological conditions usually in aggregates of anhedral grains and rarely as euhedral crystals (KULLERUD and DONNAY, 1960).

JONG (1928) was the first who determined the crystal structure of bornite by x-ray method concerning the natural specimen and proposed a structure bearing a cubic cell with $a = 10.910 \pm 0.005\text{kX}$. Based on the study of the structure of synthetic material by means of x-ray powder method, LUNDQVIST and WESTGREN (1936) gave a cubic

cell with $a = 10.94 \text{ \AA}$ and the space group $Fd3m$ composed of close-packed sulfur atoms associated with metal atoms in the interstices. TUNELL and ADAMS (1949) examined the crystals of bornite representing a cubic cell with $a = 32.8 \text{ \AA}$ from the Carn Brea Mine, Cornwall.

Recently, MORIMOTO (1961, 1964) studied the polymorphism in bornite, indicating three modifications, i.e. 1) high-temperature cubic form with $a = 5.50 \text{ \AA}$, composed of Cu_5FeS_4 , stable above $228 \pm 5^\circ\text{C}$ and changing to a transitional metastable form on cooling below $228 \pm 5^\circ\text{C}$, 2) the metastable form with $a = 10.94 \text{ \AA}$ and the space group $Fd3m$ resulted from twinning of the small domains with rhombohedral symmetry in eight different orientations, varying gradually to the low-temperature form and 3) the low-temperature form belonging to the space group $P4_21C$ with $a = 10.94$ and $c = 21.88 \text{ \AA}$.

Concerning the electric and magnetic properties, only FRUEH (1950) measured resistivity in the temperature range from 30° to 260°C along a smooth curve of decreasing values with increasing temperature up to 170°C .

So far we have tried to clarify contribution of the 3d-electrons to the electric conductivity by studying the electric, magnetic and crystallographic characters of the compounds such as FeS , CrS , CrSe , MnAs , etc. (MASUMOTO *et al.*, 1964, 1965; TAKENO *et al.*, 1966). As to the minerals belonging to the Cu-Fe-S system, TERANISHI (1961) studied the magnetic and electric properties of CuFeS_2 with antiferromagnetic and electrically semiconductive characteristics. Recently, we have examined magnetism in case of CuFe_2S_3 which is weakly ferromagnetic in orthorhombic form and ferrimagnetic at very low temperature in cubic form.

The aim of the present experiment has been to clarify the electric and magnetic properties of synthetic and natural bornites attributable to the crystal modifications described in detail by MORIMOTO (1961, 1964) and YUND and KULLERUD (1966). The results obtained have referred to disputation with respect to the physical properties of Cu-Fe-S minerals.

II. SPECIMENS USED IN THE EXPERIMENTS

A. Synthetic materials

As the starting materials for synthesis of the mineral, electrolytic copper and iron with purity of 99.9 per cent and sulfur purified twice by vacuum distillations were mixed with one another in any proper proportion. These materials were sealed in the silica glass tube held at an evacuated state (down to about 10^{-5} mmHg). The tube was inserted into an electrical furnace and kept at $600^\circ \sim 700^\circ\text{C}$ for 24 hours. To get homogeneous mixture, the product was then ground in an agate mortar with acetons to prevent oxidation, sealed again in the evacuated silica-glass tube, reheated in the furnace at 1000°C and cooled with the rate of 10°C per an hour to the room temperature.

The products obtained were subjected to identification in relation to their physical,

optical and x-ray properties. In the polished sections, bornite of Cu_5FeS_4 composition is pinkish or slightly brownish orange in color immediately after polishing. Owing to oxidation, however, its color changes rapidly to purple and later to bluish violet. The mineral is optically isotropic. As shown in Table 1, the x-ray powder data of the mineral clearly indicate the tetragonal bornite suggested already by MORIMOTO or YUND and KULLERUD.

TABLE 1. THE DATA OF X-RAY POWDER DIFFRACTION FOR
SYNTHETIC AND NATURAL BORNITE
($\text{CuK}\alpha$ radiation with Ni filter)

Synthetic Cu_5FeS_4		Synthetic $\text{Cu}_{4.9}\text{Fe}_{1.1}\text{S}_4$		Natural $\text{Cu}_5\text{Fe}_4\text{S}$ *	
dÅ	I	dÅ	I	dÅ	I
4.08	1/2	4.30	3	4.07	1/2
3.31	4	3.30	1		
3.28	1/2			3.26	3
3.175	5	3.13	1	3.15	5
2.812	2	2.806 b	1/2	2.806	2
2.738	3	2.737	1	2.739	3
2.644	1/2	2.240 b	1/2	2.515	3
2.509 b	2	2.131	1		
2.107	1	1.981	1/2	2.123	1/2
1.934	10	1.937	10	1.937	10
1.850	1/2	1.773	1/2		
1.658	1	1.655	1/2	1.653	1
1.533	1			1.535	1/2

* Natural bornite from the Shirataki mine, Shikoku. b: Broad peak.

B. Natural bornite from the Shirataki mine, Shikoku, Japan

The ore deposits of the Shirataki mine are of the 'Kieslager' type occurring in the Sambagawa crystalline schists. The constituent opaque minerals is pyrite associated with chalcopyrite, sphalerite, bornite, chalcocite, covellite, native silver and so on in small amounts. The specimens used in the experiments are found in the apophyses branching out from the stratified ore body in the schists and include a small amount of chalcopyrite laths (about 3 mol per cent) under reflection microscope. The x-ray powder data of the mineral are shown in Table 1.

III. EXPERIMENTAL PROCEDURES

The measurement of electric conductivity was carried into execution by the ordinary four-probe method, using the K-2 type potentiometer. The specimens used in these manipulations were prepared to bear a shape of rectangular parallelepiped, about $0.5 \times 1.0 \times 5.0 \text{ mm}^3$ in size, coated with gold on either terminal for making the contact

resistance least. The experiments were measured in vacuum (10^{-4} mmHg) in the temperature range between liquid nitrogen temperature and 600°C .

The measurement of magnetism was carried out by using the magnetic balance with an automatically recording instrument described in detail in the previous papers (TAKENO, 1966 and TAKENO *et al.*, 1966). The electromagnet was operated at 8000 Oe with the field gradient calibrated by Mohr's salt. The experiments were proceeded in vacuum in the range between liquid nitrogen temperature to about 500°C .

IV. RESULTS OBTAINED

A. Electric conductivity

The values for natural bornite, synthetic Cu_5FeS_4 and synthetic $\text{Cu}_{5-x}\text{Fe}_{1+x}\text{S}_4$ are shown in the figures 1, 2 and 3 respectively. In these figures, the vertical and transversal axes represent conductivity in logarithm and reciprocal absolute temperature ($1/T$) respectively.

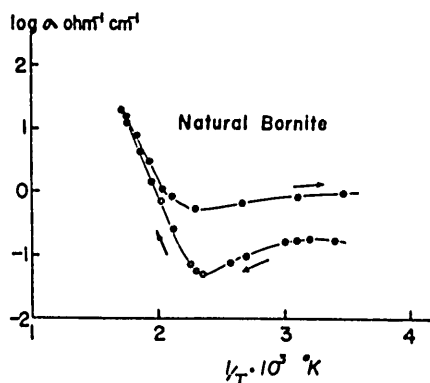


FIG. 1. Conductivity of natural bornite from the Shirataki mine, as a function of the inverse absolute temperature. The arrows show each direction for the temperature variation.

As are seen in these figures, no essential difference between the electric conductivity of natural bornite and that of synthetic one is observed. The conductivity is of order of $10^0 \text{ ohm}^{-1}\text{cm}^{-1}$ at the room temperature and increases linearly with increasing temperature, suggesting that the mineral in question is typically semiconductive. In the figures 1 and 2, two distinct anomalies are recognized and interpreted with reference to the crystal transformation alluded to already in the literatures. The one is an abrupt increase of conductivity at about 180°C ascribable to transformation from the low-temperature tetragonal form to the transitional metastable one, while the other is a step at about 300°C on the conductivity versus $1/T$ curves revealing a sort of transformation from the metastable to the high cubic form.

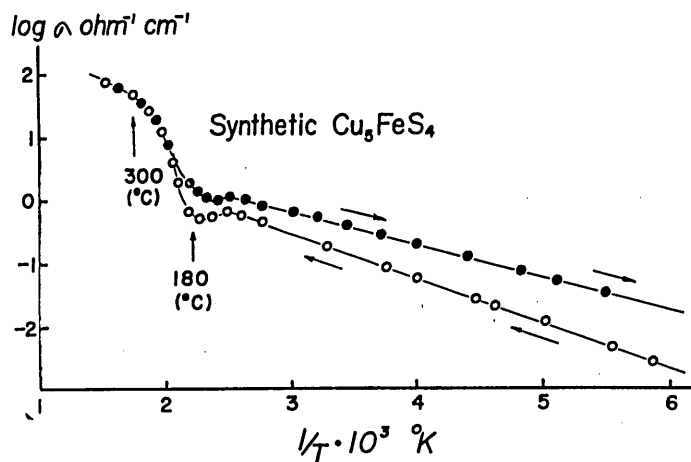


FIG. 2. Conductivity of synthetic bornite as a function of the inverse absolute temperature.

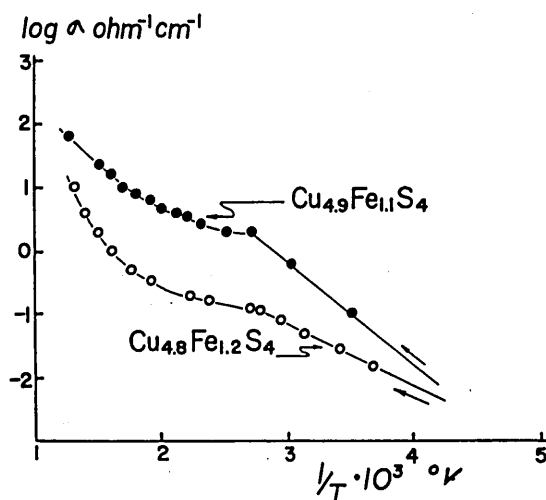


FIG. 3. Conductivities of synthetic $\text{Cu}_{4.9}\text{Fe}_{1.1}\text{S}_4$ and $\text{Cu}_{4.8}\text{Fe}_{1.2}\text{S}_4$ as a function of the inverse absolute temperature.

In these experiments, the trend of variation in value almost perfectly coincides with each other on cooling or on heating above about 180°C but does not so in the range below this temperature. The causes of these phenomena will be discussed later.

The values for the synthetic non-stoichiometric bornite are given in the figure 3. The powder patterns obtained for these materials after annealing above about 600°C exhibits the cubic structure. There appears no anomaly at about 180° and 300°C , while the breakings are observed on the conductivity versus $1/T$ curves at 98°C and 92°C for $\text{Cu}_{4.9}\text{Fe}_{1.1}\text{S}_4$ and $\text{Cu}_{4.8}\text{Fe}_{1.2}\text{S}_4$ respectively. Nevertheless, the tendency of

conductivity is almost similar to that in case of the specimen with the stoichiometric composition.

Concerning the Hall-voltage measured by the direct current method at the magnetic field of 15 KOe at the room temperature any remarkable results were not obtained because of its too small values to be detected.

B. Magnetic susceptibility

Its values per gram (χ_g) of the synthetic bornite are presented in the figure 4, showing the decrease in paramagnetic property with increasing temperature in all of the temperature range. Its value decreases abruptly at 180°C and shows a sort of breakdown at about 300°C. An anomaly at about 180°C is characterized by such a distinct thermal hysteresis that χ_g increases abruptly at 179°C on cooling but at 188°C on heating.

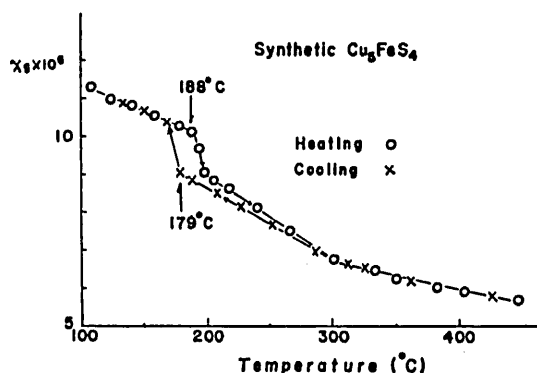


FIG. 4. Magnetic susceptibility of synthetic bornite as a function of temperature. The arrows show each direction of the temperature variation.

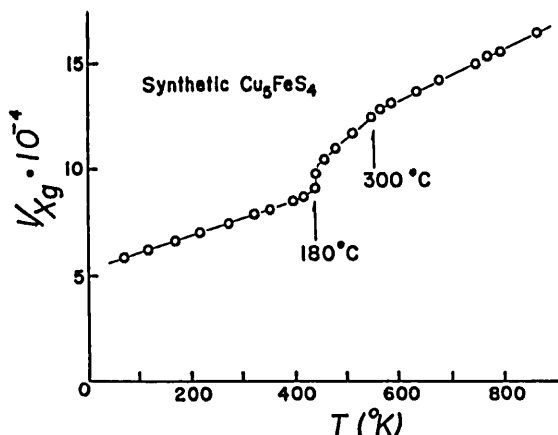


FIG. 5. The inverse susceptibility of synthetic bornite as a function of temperature.

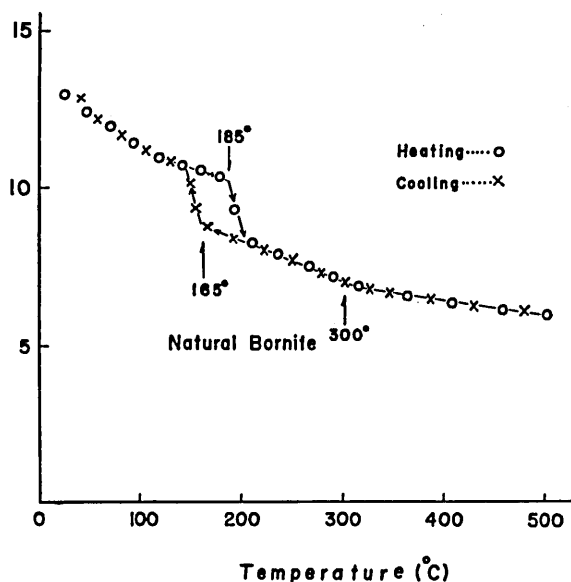


FIG. 6. Magnetic susceptibility of natural bornite as a function of temperature.

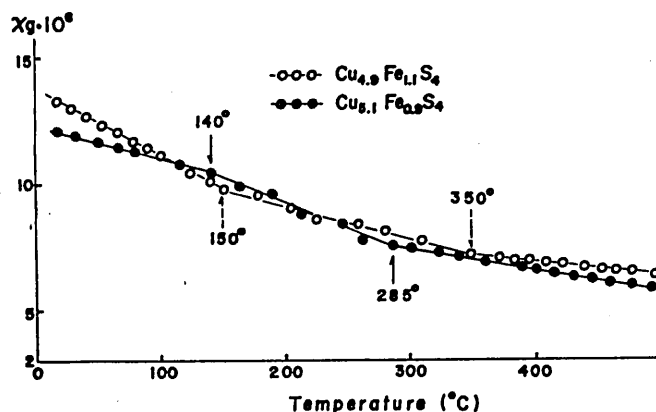


FIG. 7. Magnetic susceptibilities of synthetic $\text{Cu}_{4.9}\text{Fe}_{1.1}\text{S}_4$ and $\text{Cu}_{5.1}\text{Fe}_{0.9}\text{S}_4$ as a function of temperature.

On the other hand, variation of the inverse susceptibility for the synthetic bornite with temperature curve is $(1/\chi_g - T)$ clearly linear in the range respectively, below 180°C and above 300°C obeying the Curie-Weiss law (see, fig. 5).

Its values for the natural bornite with a tendency almost similar to that of the synthetic materials except an anomaly at about 165°C instead of 180°C in case of the latter are indicated in the figure 6.

$\chi_g - T$ curves of synthetical non-stoichiometric bornite such as $\text{Cu}_{5.1}\text{Fe}_{0.9}\text{S}_4$ and $\text{Cu}_{4.9}\text{Fe}_{1.1}\text{S}_4$, annealed above 600°C , are shown in the figure 7. Although the anomaly at about 180°C observed in the stoichiometric phase disappears, breakings on the

TABLE 2. MAGNETIC DATA FOR THE SYNTHETIC BORNITE

	Cu_2FeS_4		$\text{Cu}_{1.9}\text{Fe}_{1.1}\text{S}_4$		$\text{Cu}_{3.1}\text{Fe}_{0.9}\text{S}_4$	
	I below 180°C	II above 300°C	I below 150°C	II above 350°C	I below 140°C	II above 285°C
$P_{\text{eff.}} (\mu_B)$	5.76	6.68	4.51	6.22	5.38	4.75
$\theta_P (^\circ\text{K})$	-483	-664	-82	-672	-440	-177

susceptibility curves at 140° and 150°C are recognizable respectively.

In Table 2, the temperature range in which the Curie-Weiss law $\chi = C/(T + \theta_p)$ holds good, the effective Bohr magneton ($P_{\text{eff.}}$) and the Curie temperature (θ_p) are listed.

V. CONSIDERATIONS

In order to consider the electric and magnetic properties of bornite, it seems necessary to scrutinize the relations between bornite and Fe-S minerals (such as pyrrhotite and pyrite) and those between bornite and Cu-S minerals (such as covellite and chalcocite). The minerals mentioned above are used to occurring in an intimate association and complicated genetical connection with the bornite in nature. The phases tetragonal $(\text{Fe, Ni, Co})_{1+x}\text{S}$, rhombohedral Fe_3S_4 and cubic Fe_3S_4 are relatively rare and were not established completely, they are not considered in this paper.

The fact is that the minerals belonging to the Cu-Fe-S system are common and important in natural occurrence. However, no remarkable investigations with respect to their electric and magnetic properties, especially to those of the ternary system, have so far been given in the literatures. It is well known that their electric property is generally semiconductive but, owing to their property of extremely structure-dependence, many experimental results have not been in good harmony with the fundamental law. Electric and magnetic data given in the literatures together with our non-published data are shown in Table 3.

1. *Pyrrhotite*

Numerous investigations have hitherto been done with reference to the natural and synthetic pyrrhotite. It has been remarked that the magnetic and crystallographic properties of the mineral in question change considerably with a slight variation of its composition, and the following facts have been noticed.

In the composition range between $\text{FeS}_{1.00}$ and about $\text{FeS}_{1.07}$, the mineral is anti-ferromagnetic and $T_\beta = T_N = 320^\circ\text{C}$, $\theta_p = -875^\circ\text{K}$ and $P_{\text{eff.}} = 5.24\mu_B$, while it is electrically semiconductive and in the temperature range below $T_\alpha (140^\circ\text{C for FeS}_{1.00})$ shows an extreme anisotropy in conductivity with the order of about $10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$ along c -axis and $10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$ along a -axis respectively at the room temperature.

On the other hand, iron-deficient pyrrhotite FeS_x ($x \geq 1.07$) is of ferrimagnetic property with γ -transformation and $T_c = 305^\circ\text{C}$, $\theta_p = -1900^\circ\text{K}$ and saturation magnetization is about 17 emu/gr for $\text{FeS}_{1.14}$ (Fe_7S_8), while the mineral is electrically metallic (LOTGERING, 1965; HARALDSEN, 1937, 1941; HIRAHARA, 1958; HIRAHARA, 1960; TAKENO and TAKENO *et al.*, 1966).

2. *Pyrite*

FeS_2 has, though well known as a crystal mineral detector, not so much detailedly been investigated especially concerning its electric property. The mineral concerned is said to be diamagnetic and electrically a sort of semiconductor with about $10^0 \sim 10^2$ ohm $^{-1}\text{cm}^{-1}$ in conductivity, occurs as n- and p-type semiconductor below the room temperature in natural state but turns to an intrinsic semiconductor with 0.5~1.2eV in activation energy (KAMIGAICHI, 1956; MARINACE, 1954; HILL *et al.*, 1962; SUZUKI, 1963).

3. *Covellite and Chalcocite*

Stoichiometric CuS , covellite, electrically metallic in the range of $10^4 \sim 10^5$ ohm $^{-1}\text{cm}^{-1}$ in conductivity, occurs as n- and p-type semiconductors below about 100°C but turns to intrinsic semiconductor with 0.1~0.8eV in activation energy at high temperature. It is not clear whether the mineral in question may, though paramagnetic in order, be diamagnetic or not.

HIRAHARA (1951) investigated cuprous sulfide Cu_2S electrically in detail. He showed its two transition points at about 110°C and 470°C , of which the latter was confirmed by measuring the electric and ionic conductivity, thermal linear expansion, heat capacity, thermoelectromotive force, and so on. The mineral is definitely a p-type semiconductor at low temperature.

Concerning the Cu-S system, as were indicated by DJURLE (1958), MORIMOTO (1962), and ROSEBOOM (1962), a new mineral djurleite, $\text{Cu}_{1.96}\text{S}$, with trimorphic forms has now been determined. It is however considerably difficult to identify the mineral under consideration because of its x-ray patterns seemingly similar to those of chalcocite a slight difference in sulfur content, and optical resemblance under the reflection microscope.

4. *Chalcopyrite*

There have been few investigations for three component compounds of Cu-Fe-S as semiconductor. TERANISHI (1960) reported the electric and magnetic properties of synthetic and natural chalcopyrite. The mineral behaves as a typical semiconductor bears relatively large values in Hall mobility and thermoelectric power in spite of its content of transitional element, Fe. Moreover, the mineral is considered antiferromagnetic based on the anisotropic susceptibility of a natural single crystal along both directions around the easy axis ($1\bar{1}0$), while the susceptibility increases with increasing temperature above $T_N(550^\circ\text{C})$. It is to be noted that its behaviour is rather different

from that of the typical antiferromagnetic materials such as $\text{FeS}_{1.00}$.

In addition to chalcopyrite, SAWADA *et al.* (1962) gave the data for a magnetic property of natural cubanite, i.e. σ - T curve above the room temperature in association with those for x-ray and chemical analyses.

5. Discussion on the experimental data for cubanite and bornite

As regards the physical properties of Cu-Fe-S minerals for semiconductive substances, the writers have investigated already about those of pyrrhotite (KAMIGAICHI, 1955 and 1956; TAKENO and TAKENO *et al.*, 1966), pyrite (KAMIGAICHI, 1956) and $\text{Cu}_{1.8}\text{S}$ (KAMIGAICHI, 1952) and recently with respect to those of natural and synthetic cubanites. Some part of the results obtained were already read at some meetings of the Mineralogical Society of Japan and the Physical Society of Japan. So, we will discuss the electric and magnetic properties of CuFe_2S_3 (a paper described in detail is now in preparation) and of Cu_5FeS_4 in the following.

A. Cubanite

Cubanite is weakly ferromagnetic in natural orthorhombic form but above 245°C (T_T in Table 3) transforms to a cubic modification and behaves paramagnetically. On cooling, the magnetic susceptibility of the cubic cubanite, no matter whether synthetic or derived from the natural orthorhombic form, shows no anomaly at 245°C but increases abruptly at just the liquid nitrogen temperature and reveals a ferrimagnetic property. The detailed measurements for this kind of cubanite are now carried on. θ_p is about -3000°K for both cubic and orthorhombic forms.

Orthorhombic cubanite is a sort of semiconductor with activation energy of about 0.02eV while cubic form is metallic.

The problems remained to be confirmed are as follows:

- 1) Examination of the magnetism and the easy direction for a single crystal.
- 2) Precise measurements of the electric and magnetic properties of cubic cubanite below the liquid nitrogen temperature, i.e. the Curie temperature, saturation magnetization, electric conductivity and so on.

Moreover, it has so far been thought that the cubic cubanite and cubic chalcopyrite are isostructural with each other (e.g. GENKIN *et al.*, 1966). Therefore, we have expected that the cubic CuFeS_2 and the materials with somewhat modified chemical compositions relating to those of chalcopyrite and cubanite such as $\text{Cu}_{1.1}\text{Fe}_{0.9}\text{S}_2$, $\text{Cu}_{0.9}\text{Fe}_{1.1}\text{S}_2$ etc or $\text{Cu}_{1.1}\text{Fe}_{1.9}\text{S}_3$, $\text{Cu}_{0.9}\text{Fe}_{2.1}\text{S}_3$ etc. indicate the ferrimagnetic nature at about the liquid nitrogen temperature but have not reached the satisfactory results, since the ferrimagnetic nature has not been observed for any cubic specimens (annealed at about 600°C) other than stoichiometric CuFe_2S_3 .

B. Bornite

It seems that its magnetic and electric properties are in a very close relation to the crystal transformations. The first transformation appears at about 180°C and a differ-

TABLE 3. ELECTRIC AND MAGNETIC DATA FOR Cu-Fe-S MINERALS

Mineral Name	Chemical Composition	Crystal Structure	Electrical Properties			Magnetic Properties					References
			Conductivity at room temperature (ohm ⁻¹ cm ⁻¹)	Type of conduction	Activation Energy (eV)	Type of magnetism	T _N or T _C (°C)	Paramagnetic Curie Temperature -θ _p (°K)	Magnetic moment		
									Ferro. (σs/gr)	Paramag. Peff. μ _B	
Pyrrhotite	FeS _{1.00~1.07}	Hexagonal	10 ¹ ~10 ²	Semicon.	0.05~0.08	Antiferro.	T _N =320	875	—	5.24	Hihara (1960)
	FeS _x (x>1.07)	{Hexagonal Monoclinic	10 ³	Metallic	—	Ferrimag.	T _C =305	1900	17	5.93	Hirahara (1958)
Pyrite	FeS ₂	Cubic	10 ⁰ ~10 ²	Semicon.	0.5~1.2	Diamag?	—	—	—	—	Marinace (1954)
Covellite	CuS	Hexagonal	10 ⁴	Metallic	—	Paramag.	—	—	—	—	Kamigaichi (1952)
Chalcocite	Cu ₂ S	Orthorhombic	5.5×10 ¹	Semicon.	0.06	Diamag?	—	—	—	—	Hirahara (1951)
Chalcopyrite	CuFeS ₂	Tetragonal	0.8~2.0×10 ¹	Semicon.	imp. 0.03 int. 1.3	Antiferro.	T _N =550	~	—	3.85	Teranishi (1961)
Cubanite	CuFe ₂ S ₃	Orthorhombic	6.8×10 ⁻²	Semicon.	0.02	weak Ferromag.	T _T =245	3000	1.0	—	
		Cubic	5.7×10 ¹	Metallic	—	(Ferri.) Paramag.	T _C =-182		?	6.7	
Bornite	Cu ₅ FeS ₄	Tetragonal	2.1~3.0×10 ⁻¹	Semicon.	0.25~0.35	Paramag.	—	483	—	5.76	
		Cubic			0.54		—	664	—	6.68	

ence in conductivity between the low temperature phase (phase I in Table 2) and the high temperature one (phase II in Table 2) is to be remarked.

The decrease of the electric conductivity in the temperature range of $100^\circ\sim 180^\circ\text{C}$ resembles that appears when impurity conduction is disturbed by thermal scattering. In the case of bornite, however, the decrease may be ascribed to scattering of the carrier of electrons in connection with local transformation of the crystal structure (see, figures 1, 2 and 3).

Moreover, disagreement of the conductivity of the low temperature phase on cooling is of course due to a sensitive structure-dependence. For instance, it may come from the irregularity, strain and distortion of the crystal appearing at the transformation temperature. It seems also possible that restriction of the band gap ascribed to the barrier of impurity levels makes the values of activation energy and that the alteration of the surface of the specimen gives some effects on conductivity.

As far as the electric and magnetic properties are concerned, there seems no essential difference between natural and synthetic materials.

As is seen in Table 2, the paramagnetic Curie temperature of the low-temperature tetragonal phase appears at -664°K , and it is presumable that the mineral is antiferromagnetic, revealing Néel point below the liquid nitrogen temperature. Further, the Bohr-magneton number of this phase is estimated $6.68\mu_B$ larger than $5.90\mu_B$, the theoretical one, calculated from assumption that the mineral is composed of $\text{Cu}_5^+\text{Fe}^{3+}\text{S}_4^{--}$ (BATES, 1951). This disagreement may also be attributed to postulation that the mineral partly contains Fe^{++} and Cu^{++} . If so, it may be that the ferrimagnetic nature appears at a very low temperature (lower than the liquid nitrogen temperature).

Considering the experimental data and discussions described in the preceding, it can be concluded that the following experiments are to be closely connected with the detailed scrutiny either on the electric and magnetic properties of the semiconductive bornite in the temperature range below the liquid nitrogen temperature or on the effects of addition of some impurities.

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REFERENCES

- ALLEN, E. T. (1916): The composition of natural bornite. *Am. J. Sci.*, **41**, 409-413.
 BATES, L. F. (1951): *Modern Magnetism*. Cambridge Univ. Press, Oxford, pp. 151.
 DJURLE, S. (1958): An x-ray study on the system Cu-S. *Acta Chemica Scand.*, **12**, 1415-1426.
 FRUEH, A. J. Jr. (1950): Disorder in the mineral bornite. *Am. J. Sci.*, **35**, 185-192.
 GENKIN, A. D., FILIMONOVA, A. A., SHADLUN, T. N., SOBOLEVA, S. V., and TRONEVA, N. V. (1966): On cubic cubanite and cubic chalcopyrite. (in Russian). *Geol. Rudn. Mest.*, **8**, 41-54.
 HARRINGTON, B. J. (1903): On the formula of bornite. *Am. J. Sci.*, **16**, 151-154.
 HIIHARA, T. (1960): Magnetic and electrical properties of iron sulfide single crystals. *J. Sci. Hiroshima Univ., Ser. A.*, **24**, 31-53.

- HILL, P. A., and GREEN, R. (1962): Thermoelectricity and resistivity of pyrite from Renison Bell and Mt. Bishoff, Tasmania. *Econ. Geol.*, **57**, 579-586.
- HIRAHARA, E. (1951): The physical properties of cuprous sulfides-semiconductors. *J. Phys. Soc. Japan*, **6**, 422-427.
- , (1951): The electrical conductivity and isothermal Hall effect in cuprous sulfide, semiconductor. *Ibid.*, **6**, 428-437.
- HARALDSEN, H. (1937): Magnetochemical investigation XXIV. A thermomagnetic investigation of the transformations in troilite-pyrrhotite portion of iron-sulfide system. *Z. Anorg. Allgem. Chem.*, **231**, 78-86.
- , (1941): The high-temperature transformations of iron (II) sulfide mixed crystals. *Ibid.*, **246**, 195-226.
- JUZA, R., BILTZ, W., and MEISEL, K. (1932): The systematic doctrine of affinity LVII. The phase diagram of pyrite, pyrrhotite, troilite and sulfur vapor, criticized in view of sulfur vapor pressure, x-ray diagrams, densities and magnetic measurements. *Ibid.*, **205**, 273-286.
- KAMIGAICHI, T. (1952): Electrical conductivity of Cu_{1-x}S (Cu_9S_5). *J. Sci. Hiroshima Univ., Ser. A*, **16**, 325-330.
- , (1955): Electrical property of iron sulfide system (I). (in Japanese). *J. Educat. Study Hiroshima Univ., Part 2*, **3**, 47-51.
- , (1956): Electrical property of iron sulfide system (II) (in Japanese). *Ibid.*, **4**, 31-36.
- , (1956): Electrical conductivity and thermo-electric power of FeS_x (Pyrrhotite). *J. Sci. Hiroshima Univ., Ser. A*, **19**, 499-505.
- KULLERUD, G., and DONNAY, G. (1960): A second find of euhedral bornite crystals on barite. *Am. Miner.*, **45**, 1062-1068.
- LOTGERING, F. K. (1956): On the ferrimagnetism of some sulfides and oxides. *Philips Res. Rept.*, **11**, 190-249.
- MARINAGE, J. C. (1954): Some electrical properties of natural crystals of iron pyrite. *Phys. Rev.*, **96**, 593.
- MASUMOTO, T. (1964): Electrical conductivity of chromium selenides. *J. Sci. Hiroshima Univ., Ser. A*, **27**, 87-91.
- , and KAMIGAICHI, T. (1965): Magnetic susceptibility of chromium selenides. *Ibid.*, **29**, 47-52.
- MORIMOTO, N., and KULLERUD, G. (1961): Polymorphism in bornite. *Am. Miner.*, **46**, 1270-1282.
- , (1962): Djurleite, a new copper sulfide mineral. *Miner. Jour.*, **3**, 338-344.
- , (1964): Structures of two polymorphic forms of Cu_3FeS_4 . *Acta Cryst.*, **17**, 351-360.
- ROSEBOOM, E. H. JR. (1962): Djurleite, $\text{Cu}_{1.06}\text{S}$, a new mineral. *Am. Miner.*, **47**, 1181-1184.
- SAWADA, M., OZIMA, M., and FUJIKI, Y. (1962): Magnetic properties of cubanite (CuFe_2S_3). *J. Geomag. Geoelect.*, **14**, 107-112.
- SUGAKI, A., and SHIMA, H. (1965): Synthetic sulfide minerals (II). *Mem. Fac. Eng. Yamaguchi Univ.*, **15**, 33-47.
- SUZUKI, T. (1963): On the thermoelectric potential of pyrite. *Sci. Rept. Tohoku Univ., Ser. 3*, **8**, 317-419.
- TAKENO, S. (1966): Magnetometric and röntgenometric studies of pyrrhotite from the Kawayama mine, Japan. *J. Sci. Hiroshima Univ., Ser. C*, **5**, 113-156.
- , MASUMOTO, K., and KAMIGAICHI, T. (1966): Relation between magnetic properties and chemical compositions of natural pyrrhotite (in Japanese). *J. Miner. Soc. Japan*, **7**, 26-42.
- TERANISHI, T. (1961): Magnetic and electrical properties of chalcopyrite. *J. Phys. Soc. Japan*, **16**, 1881-1887.
- TUNELL, G., and ADAMS, C. E. (1949): On the symmetry and crystal structure of bornite. *Am. Miner.*, **34**, 824-829.
- YUND, R. A., and KULLERUD, G. (1966): Thermal stability of assemblages in the Cu-Fe-S system. *J. Petr.*, **7**, 454-488.

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