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Electric and Magnetic Properties of Cubanite

By

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with 6 Text-figures

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Abstract: The electric and magnetic properties of natural and synthetic cubanite were investigated. The electric conductivity of natural cubanite increases with increasing temperature and shows an anomalous change at 245°C, where transformation from the low temperature orthorhombic form to the high temperature cubic one is assumed to appear, and the mineral behaves as a typical semiconductor in the low temperature range but as a metallic conductor above the polymorphic transition temperature. The conductivity of synthetic cubanite is metallic in the whole temperature range measured.

Cubanite in natural orthorhombic form is weakly ferromagnetic (e.g., 1.40 emu/gr, equivalent to 0.34 μ_B/mol, at 25°C) but behaves paramagnetically above the transition temperature. No matter whether it may be synthetic or derived from the natural orthorhombic form, the cubic cubanite shows no anomaly in magnetic susceptibility at 245°C on cooling but increases its value abruptly just at the liquid nitrogen temperature and displays a ferrimagnetic property. Natural cubanite is easily magnetizable along the *b*-axis.

This is the first report of the ferrimagnetic character of a compound within the Cu–Fe–S system that was observed at the low temperature, and the origin of the ferromagnetism is discussed in relation to the crystal structure.

Contents

I. Introduction

Some compounds such as chalcopyrite, bornite and cubanite belonging to the system Cu–Fe–S are of considerable interest to the solid state physicist and mineralogist because of their characteristics as semiconductors containing the magnetic element, iron, as a principal component. However, there has been little research to date concerning the magnetic and electrical properties of these phases.

Cubanite, in accessory amounts as commonly found in ore deposits formed at the high temperature, is commonly in association with chalcopyrite, pyrrhotite and pentlandite (Schwarz, 1927; Ramdohr, 1940, 1969). Its crystal structure was investigated by

Buerger (1945 and 1947) and AZAROFF and BUERGER (1955) and defined as orthorhombic, belonging to the space group Pcmn, where $a=6.46$, $b=11.17$ and $c=6.23$ Å and containing 4 mole per unit cell. The structure is based upon a hexagonal close-packed network of sulfur atoms with both iron and copper atoms in tetrahedral coordination. BUERGER (1945) suggested that its ferromagnetism may be a result of the coordination of iron.

The thermal stability of this mineral has been investigated by several investigators (cf. SCHWARZ, 1931; BORCHERT, 1934; SAWADA *et al.*, 1962 and YUND and KULLERUD, 1966). According to YUND and KULLERUD, cubanite with the composition of $CuFe_2S_3$ is cubic in the presence of vapor above 252±3°C, tetragonal from this temperature to approximately lower than 213°C, and orthorhombic at lower temperatures. All natural cubanite, with few exceptions (e. g. GENKIN *et al.*, 1966), bear this low-temperature structure. In the study of magnetic properties, SAWADA *et al.*, (1962) found cubanite is weakly ferromagnetic and transforms from the orthorhombic to the cubic form at 270°C, but failed to observe the intermediate tetragonal form. FLEET (1970) suggested that the tetragonal phase is a mixture of the ordinary orthorhombic cubanite with the cubic modification.

In an attempt to clarify the contribution of the 3-d electrons to the electric conductivity of the compounds in the Cu–Fe–S system, the electric and magnetic properties of cubanite have been studied in this paper and the results are discussed with respect to its crystal structure.

II. EXPERIMENTAL METHODS

A. SPECIMENS PROVIDED FOR THE EXPERIMENTS

As the starting materials for synthesis of the mineral, copper and iron prepared electrically with purity of 99.999 percent 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). After heating at 700°C for about 100 hours, the product was then ground in an agate mortar with toluene to get homogeneous mixture, sealed again in the evacuated silica-glass tube, reheated at 650°C for 200 hours and cooled with the rate of 10°C per an hour. X-ray powder data of the synthetic material clearly indicate production of the cubic cubanite with the spacings at 3.06, 2.648, 1.875 and 1.596 Å which was reported already by GENKIN *et al.* (1966).

The specimens of the natural orthorhombic cubanite sampled from the Komori mine (vein-type deposit), Kyoto and Mihara mine (contact pyrometasomatic deposit), Okayama, Japan together with those of the single crystals from Sudbury, Ontario kindly provided by Dr. J. D. SCOTT of Department of Mineralogy, Queen's University, Canada were also investigated magnetically. The crystals, platy in habit, and the cleavage planes were determined through X-ray diffraction analyses.

B. ELECTRICAL AND MAGNETICAL EXPERIMENTS

For measuring the magnetism, a sort of the magnetic balance with an automatic recording instrument described previously in detail (TAKENO, 1966) was used. Measurements of the electric conductivity were carried into execution by the ordinary four-probe method, using the K–2 type potentiometer. The specimens used in the manipulations were prepared to bear a rectangular parallepiped shape and coated with gold on either terminals for making the contact resistance least. The experiments were carried out in vacuum (10^{-5} mmHg) at the liquid-herium temperature to 600°C.

III. RESULTS

A. ELECTRICAL MEASUREMENTS

The values obtained for the natural cubanite and the synthetic CuFe$_2$S$_3$ are shown respectively in the figures 1 and 2, representing the relation of conductivity to the reciprocal value of absolute temperature. As is obvious in the figure 1, conductivity of the natural

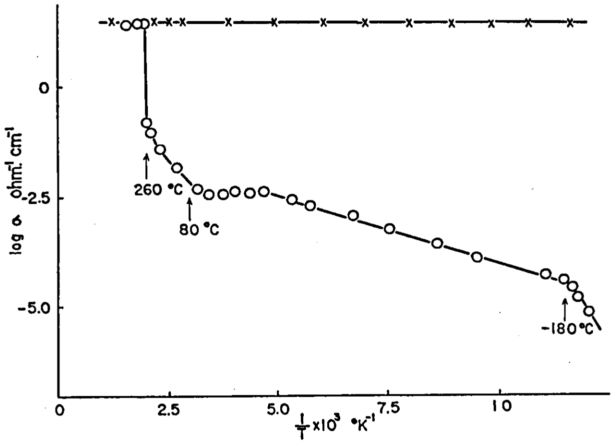

FIG. 1. Conductivity of the natural cubanite from Sudbury, Ontario as a function of the inverse absolute temperature.

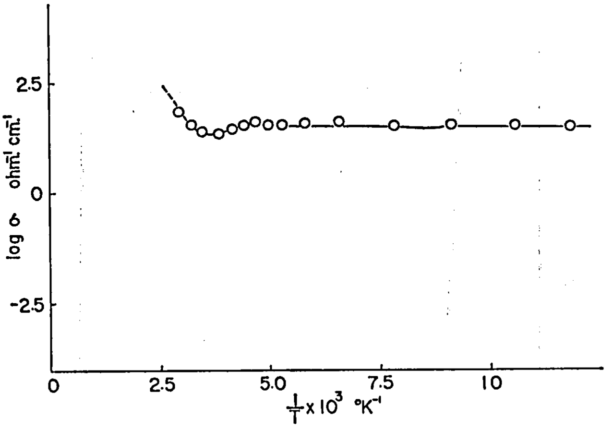

FIG. 2. Conductivity of the synthetic cubic CuFe$_2$S$_3$ as a function of the inverse absolute temperature.

cubanite is of order of 10^{-3} ohm^{-1} cm^{-1} at the room temperature and increases gradually with increasing temperature, suggesting that the mineral in question is typically semiconductive. At about 240°C to 260°C conductivity abruptly increases and avobe this temperature the value is kept almost constant with increasing temperature, pointing to a sort of metallic property. Below about -180°C, it remarkably decreases with decreasing temperature and behaves as that almost like an insulator. Below the phase transition temperature, the respective curves obtained through cooling, reheating and recooling are well agreeable with one another, whereas heated once above about 240°C, the cooling curve coincides with that of the synthetic cubic cubanite. The phase transition temperature, 245°C, is in a good agreement with that obtained from the thermo-magnetic curve, which will later be described.

Activation energy estimated from log σ–$1/T$ curve is 0.073 eV between -170° and 100°C and 0.44 eV between 80° and 200°C.

B. MAGNETIC MEASUREMENTS

The data for saturation magnetization of the natural cubanite as a function of temperature under the magnetic field of 7.2 kOe are given in the figure 3, wherein the arrows show the direction of heating (cooling). As is seen in the figure, the natural orthorhombic cubanite is weakly ferromagnetic (1.40 emu/gr at 25°C) and intensity of its magnetization is held almost constant with increasing temperature up to about 245°C, the temperature of transformation to the cubic form. At this temperature it indicates a sudden decrease of magnetization and at the higher temperature behaves paramagnetically. In the case of cooling the specimen heated above 245°C, the curve shows no anomaly at the temperature of the polymorphic transition to the orthorhombic form but the paramagnetic feature. On cooling below the room temperature, the cubic cubanite reveals weakly ferromagnetism just below the liquid-nitrogen temperature. The data for saturation magnetization of the synthetic $CuFe_2S_3$ are plotted in the figure 4 showing that the maximum value of the ferromagnetic magnetization of the cubic cubanite at -218°C is 7.2 emu/gr (equivalent to 0.34 Bohr magnetons/mol). This ferromagnetic property of the cubic phase was confirmed concerning both the synthetic cubanite and the cubic

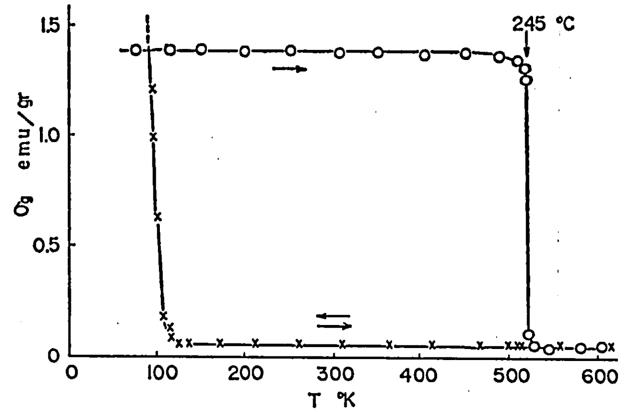

FIG. 3. Magnetization of the natural cubanite as a function of temperature.

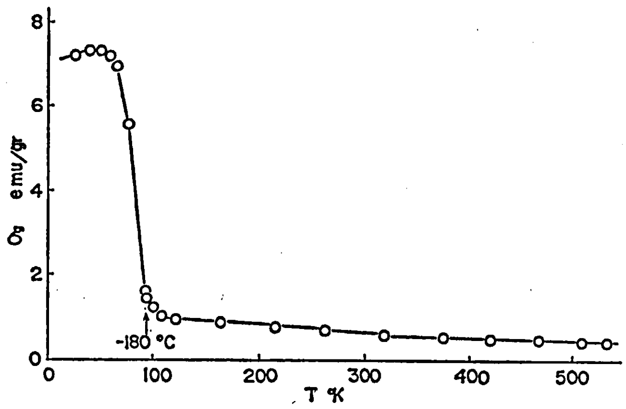

Fig. 4. Magnetization of synthetic cubic $CuFe_2S_3$ as a function of temperature.

cubanite derived from the natural orthorhombic cubanite, but was not observable in the natural orthorhombic cubanite. For reference, the value of 7.2 emu/gr corresponds to that for the hexagonal pyrrhotite (~11C-type, $Fe_{10}S_{11}$ of Nakazawa and Morimoto, 1971). In addition, attempts to observe the ferromagnetic property at very low temperature in several synthetic compounds with somewhat modified chemical composition related to those of chalcopyrite and cubanite have not been successful. Even in the case of the synthetic chalcopyrite isostructural with the cubic cubanite, the similar property has not been ascertained.

Owing to minuteness of the single crystal and the very minute scale of impurities of Fe–S phases in the synthetic materials used in these experiments, accuracy of the values in the paramagnetic region was not obtainable. However, the paramagnetic Curie temperature (θp) was determined as −700°K through application of the Curie-Weiss law.

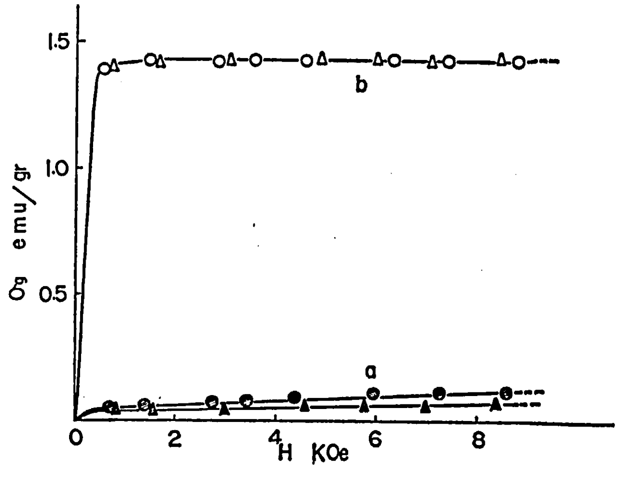

Fig. 5. Magnetic field dependence of magnetization of the natural single crystal of cubanite (circles: at 25°C and triangles: at 77°K).

The data for the magnetic field dependence of the natural single crystal of cubanite at the room temperature and at 77°K are shown in the figure 5, wherein the ordinate represents magnetization per gram and the abscissa the strength of the magnetic field and the symbol "a" represents an orientation parallel to the *a* and *c* axes (010) and "b" that parallel to the *b* axis. The crystal provided for measurement is platy in habit ($3\times 2\times 1\ mm^3$). As is apparent in the figure, the crystal is considered fully saturated in a magnetic field of 700 Oe along the *b* axis but not magnetized along the *a* and *c* axes even in a magnetic field of 8000 Oe. This magnetically anisotropic orientation is kept invariably with increasing temperature up to the polymorphic transition temperature.

IV. DISCUSSION

The writers have already discussed significance of the physical properties of the sulfide minerals belonging to the system Cu–Fe–S and summarized the electric and magnetic properties of these compounds (TAKENO, MASUMOTO and KAMIGAICHI, 1968). The compounds in question are in general electrically semiconductive but it is common owing to their sensitive structure-dependence that the experimental data have not been in good harmony with those derived from the fundamental law and it is also the case with cubanite.

As has already been stated, the orthorhombic cubanite is typically semiconductive in electric property and this fact is reasonably explained with reference to the crystal structure of the mineral proposed by FLEET (1970). The ionic character is, as the result of ordering of iron and copper atoms (figure 6), probably prevalent in the crystal structure, resulting in a semiconductive characteristics. In the structure of the cubic modification, however, the cations are so randomly distributed as to derive a metallic property from dominancy of the "direct exchange interaction" among the metallic atoms.

Since the first report on the ferromagnetic property of cubanite by BUERGER (1945), this mineral has been the subject of studies by both physicists and mineralogists. With respect to the origin of the weak ferromagnetism of the orthorhombic cubanite, BUERGER proposed that the structural peculiarity of the iron atoms associated together in pairs across the shared tetrahedral edges is doubtless concerned with ferromagnetism of the crystal under consideration. FLEET suggested that the paramagnetic iron atoms are arranged in two magnetic sublattices in such a way that in the "ideal" state the crystal is as a whole antiferromagnetic, but the close proximity of the iron atoms may result in magnetic moment due to interaction of the electron spins. The saturation magnetization of the mineral was estimated 0.87 emu/gr by SAWADA *et al.* (1962), although this value is so small compared with that of the present result (1.40 emu/gr). It seems that difference between these data is attributed to the specimens, since the powdered specimens were provided in the former case and the single crystals in the latter, and in addition, the present data were taken along the direction of the spontaneous magnetization of the very crystal.

The result of the present investigations indicates that the weak ferromagnetism of the orthorhombic cubanite may be explained on the basis of the theory proposed by DZYALOSHINSKY (1958) and by MORIYA (1963). As is conspicuous the figure 6, two sublattices in a unit cell of cubanite are supposed along the *b* axis and each sublattice has three alignments of the metal atoms along the *c* axis. Within the structure, iron atoms are arranged on every three layers producing the antiferromagnetic coupling of the magnetic moment,

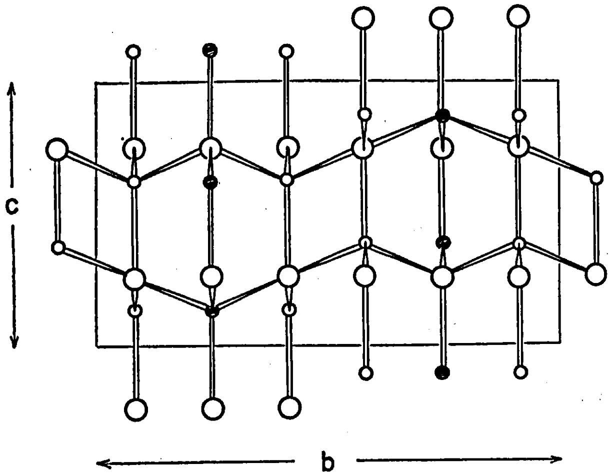

FIG. 6. The ideal structure of cubanite. S: large open circles; Fe: small open circles; Cu: small stippled circles (after FLEET, 1970).

and the weak ferromagnetism of cubanite may be attributed to this property accompanying a kind of "cant" along the *b* axis.

To be noted is that the crystal shows a remnant magnetization associated with a memory phenomenon just like that in the case of αFe_2O_3.

As is recongnized from the fact that magnetization of the orthorhombic cubanit does not decrease up to the transition temperature (see figure 3), the antiferromagnetic coupling is so strong that NÉEL temperature of the mineral is confirmable at the higher temperature. In the case of cubanite, however, the crystallographic transition occurs far below the hypothetical NÉEL temperature and the antiferromagnetic coupling disappears in the structure of the cubanite above the transition temperature. As was already mentioned, the transition of the high-temperature cubic structure is not reversible even at the considerable slow rate of cooling. It is probably possible that the measurements below 245°C were performed on the metastable cubanite. Within a reasonable duration of time, the structure of the cubic cubanite is held stably and it is worth discussing the magnetic mechanism of this phase.

As for the origin of the weakly ferromagnetic property of the cubic cubanite, it is difficult to apply the Moriya's theory because there is nowhere any ordering of the metal atoms in the unit cell of the cubic form. σ_g–T curve of the cubic cubanite below $-180°C$ corresponds to that of the "P–type" given by NÉEL (1948) and subsequently observed in the compound of (Ni, Mn, Ti)-ferrite. The spontaneous magnetization increases with increasing temperature, its maximum point in the case of the cubic cubanite being just below the liguid-nitrogen temperature, and the phenomena being due to the abnormal decrease of the spontaneous magnetization of one of a pair of the sublattice. The weakly ferromagnetic property of the cubuc cubanite is therefore interpretable after the theory proposed by NÉEL but not after that of MORIYA. However, for emergence of the ferrimagnetism, a kind of super structure is considered indispensable in the crystal structure. In relation to this, HALL and ROWLAND (1972) have recognized the super structure property in some minerals such as mooihoekite ($Cu_9Fe_9S_{16}$) and haycockite ($Cu_8Fe_{10}S_{16}$), which are structurally similar to chalcopyrite and talnakhite ($Cu_{18}Fe_{16}S_{32}$) (HALL and GABE, 1972). Considering that the powder diffraction pattern of the cubic cubanite is similar to that of sphalerite and that mooihoekite and haycockite bear also the sphalerite-like structure, the superstructure is to be expected in the cubic cubanite, although this has not been reported to date. If the cubic cubanite has a superstructure just like that of mooihoekite and haycockite, its chemical composition may show excess in metal or deficiency in sulfur and the compositional change to the side of sulfur deficiency could possibly be a result of the heat treatment where the cubanite, in giving off sulfur to form an equilibrium vapor phase, actually becomes depleted in sulfur to a small extent.

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