manifested as $\partial T_s/\partial H$, the field dependence of the transition temperature. Thus if one observes the magnetization as a function of field strength for a temperature $T_1$ near, but on the antiferromagnetic side of the transition, the magnetization will be nearly constant until the transition temperature $T_s$ is lowered sufficiently by the field, then an abrupt and rapid increase in magnetization will occur as the transition temperature $T_s$ is depressed below $T_1$.

T. OHOYAMA: Are there no vacant sites in the lattice?

H. S. JARRETT: We do not believe there are any vacancies in the structure. X-ray density and measured density are in good agreement.

G. DONNAY: Would an X-ray crystallographer, without help from neutron diffractions, have been able to account in some way for the observed first order transition?

H. S. JARRETT: He would have seen discontinuous change in lattice dimensions, and hence would have realized a first order phase change had taken place. He would not have observed a symmetry change, which is another criterion for a first order phase change. Thus we have, as far as I know, the first well-authenticated case of a first order phase change without a crystallographic symmetry change. As you point out the symmetry change that must occur is in the spin ordering.

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# Magnetic and Electric Properties of Chalcopyrite

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The magnetic torque, powder susceptibility and their temperature dependences of a natural single crystal of chalcopyrite are measured. The Néel temperature, the direction of antiferromagnetism and two principal susceptibilities, $\chi_\perp$ and $\chi_{/\!/}$, are obtained. These results suggest that chalcopyrite is a typical antiferromagnetics.

From results of measurements of conductivity, Hall coefficient, thermoeletric power and photoconductivity it is considered that this material is a semiconductor with a rather large energy band gap.

The crystal structure, the electronic states of constituent elements, magnetic and electric properties are considered together and it is concluded that the 3*d*-shell in this material is independent of the valence bond which consists of $sp^3$ bond.

## 1. Introduction

Chalcopyrite which has a chemical formula, $CuFeS_2$, has been known as a semiconductor with its rectifying property. This material is a very interesting semiconductor, since it contains typical magnetic ion, $Fe^{(+)}$, as a component.

Recently Donnay et al.[1] determined crystal and magnetic structure by neutron diffraction. According to them chalcopyrite was antiferromagnetic at least at room temperature. The magnetic moment of iron and copper were $3.85\,\mu_B$ and $0\pm0.2\,\mu_B$, respectively.

The ionic state and electric properties of this material were examined by some investigators[2-7]. From the consideration of large thermoelectric power and temperature dependence of conductivity they considered that chalcopyrite was an intrinsic semiconductor and the energy band gap was more than 0.5 eV. But there remains some uncertainties about the type of conduction carrier, the value of energy band gap and especially about the relation between magnetic and electric properties. We made more detailed measurements on the natural single crystal and synthetic specimen. Though the value of magnetic moment is not consistent with the consideration of band scheme, the compatible results about the type of conduction carrier and the value of energy band gap are obtained. And some discussions on the band structure of this material are given in consideration of crystal structure, electronic states of constituent elements, phase diagram and experimental results of magnetic and electric properties.

## 2. Specimen and Experimental Procedure

A large natural single crystal which was found at Arakawa Mine, Japan, was used. According to chemical analysis this crystal contains such amounts of each element as expressed by chemical formula $Cu_{1.00}Fe_{1.08}S_{2.01}$ and 0.90 wt. % of insoluble matter. The synthetic specimen was obtained by a direct reaction of constituent elements in a evacuated silica tube.

The magnetic torque was measured by a torque magnetometer and the susceptibility by a Sucksmith's type magnetometer. For the electric measurements thin platinum wires were attached to the specimen as electrodes by the method of current discharge.

All measurements were performed in a evacuated tube.

## 3. Experimental Results

Fig. 1 shows the torque curves in a magnetic field of 10200 Oe measured at −172°C and 20°C for a disc parallel to (110)-plane. The easy direction is [1$\bar{1}$0]. The variation of maximum torque with the square of magnetic field strength is linear as shown in Fig. 2. The temperature dependence of maximum torque is illustrated in Fig. 3. The maximum torque vanishes at about 550°C.

The powder susceptibility, $\chi_p$, increases with the rising temperature from liquid nitrogen temperature and continues to increase above

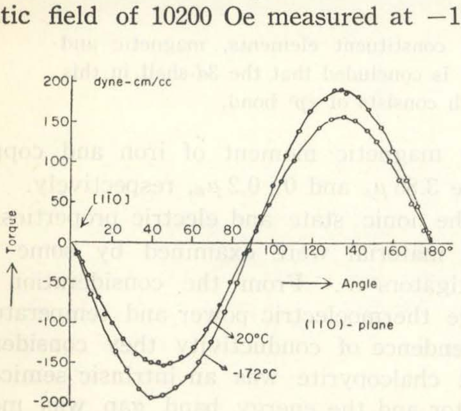

Fig. 1. Torque curves at liquid nitrogen temperature and room temperature.

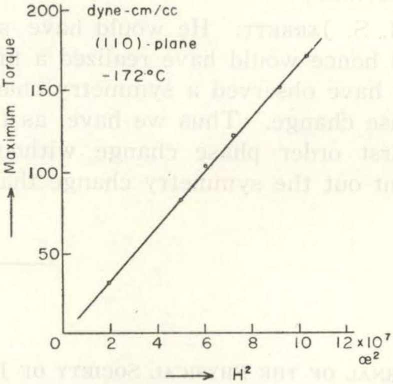

Fig. 2. The curve of maximum torque versus square of the magnetic field strength.

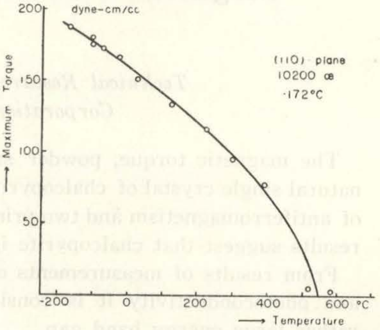

Fig. 3. Temperature dependence of maximum torque.

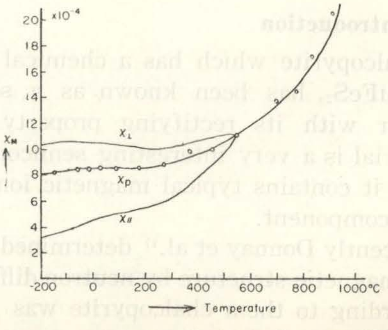

Fig. 4. Temperature variations of susceptibilities.

550°C. (Fig. 4). Therefore, unfortunately it is not able to calculate the magnetic moment from $1/\chi - T$ curve. From the powder susceptibility and the torque we can calculate two principal susceptibilities, $\chi_\perp$ and $\chi_{//}$. Their temperature variations show general behaviours of those of antiferromagnetics as shown in Fig. 4.

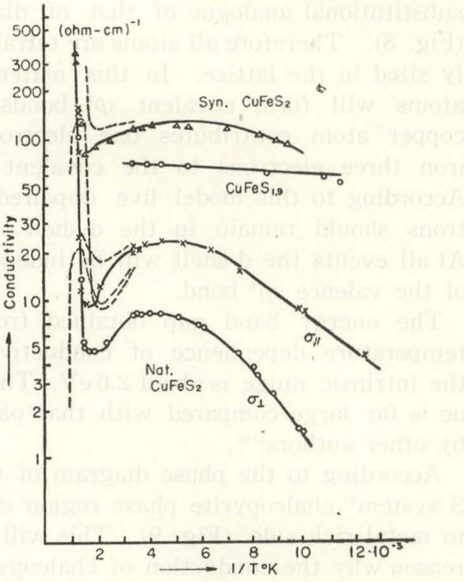

Fig. 5. Temperature variations of electric conductivities.

Fig. 6. Temperature variations of Hall coefficient and numbers of conduction carriers.

In Fig. 5 temperature variations of electrical conductivities are shown together with the results obtained by Boltaks[4] which is illustrated by dotted curves. Behaviours of our measurements resemble to that of a typical semiconductor. That is, it seems that an intrinsic conduction occurs in the temperature range beyond 300°C and impurity conduction in the range below −50°C. The results of Hall effect measurements are illustrated in Fig. 6 and Fig. 7. The mobility of conduction carriers reaches 35 cm²/volt-cm at liquid nitrogen temperature.

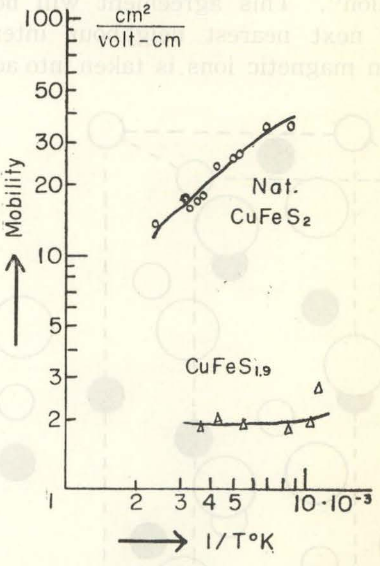

Fig. 7. Temperature variations of Hall mobilities.

The thermoelectric power is about 480 $\mu$V/deg. at room temperature. The sign is negative and agrees with that obtained from Hall effect measurement. Then the conduction of chalcopyrite is of N-type.

The photoconductivity can be observed only at liquid nitrogen temperature. The maximum of photocurrent exists at about 0.52 $\mu$ of the wave length of incident light.

## 4. Discussion

From the results of magnetic measurements it is concluded that chalcopyrite is an antiferromagnetic substance with the Néel temperature at about 550°C. At this temperature there is a crystal structure transition from chalcopyrite structure to calcium fluoride structure[8]. But taking into consideration the gradual decrease of the magnetic torque with the rising of temperature to 550°C, we shall be able to consider that the temperature 550°C is the Néel temperature. The continuous increasing of powder susceptibility even above 550°C is probably due to the decomposition of the specimen into other substances one of which has a large magnetic susceptibility (for example, FeS).

Nevertheless, using this Néel temperature and the susceptibility perpendicular to c-axis we can estimate the spin quantum number of the magnetic ion. Then we get S=3/2 as the most appropriate value which is just the same with that obtained from the neutron diffraction[1]. This agreement will not hold if the next nearest neighbour interaction between magnetic ions is taken into account.

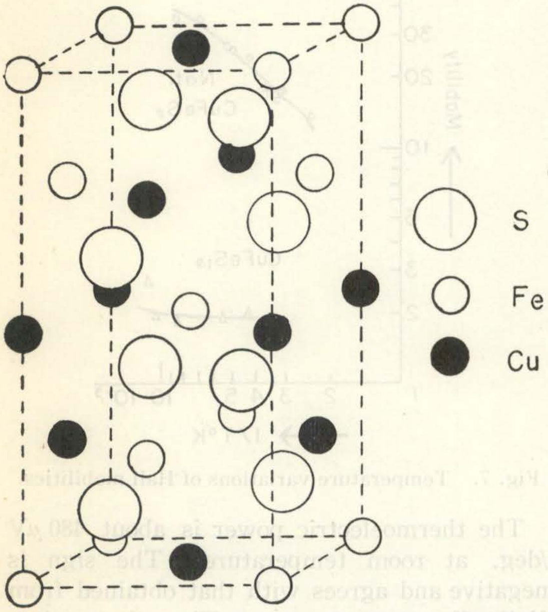

Fig. 8. Crystal structure of chalcopyrite. Large open circles represents sulphur atoms, small open circles iron atoms and small black circles copper atoms.

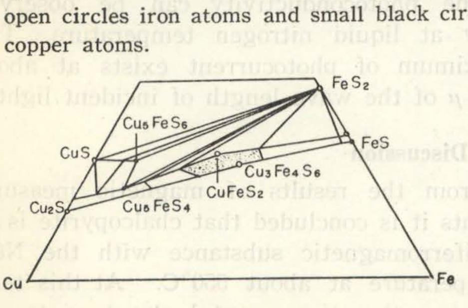

Fig. 9. Phase diagram of Cu-Fe-S system after Merwin and Lombard.[9]

From the resultes of electric measurements we can consider that chalcopyrite is a semiconductor. It should be noticed that rather large thermoelectric power, 480 μV/deg., large electron mobility, 35 cm²/volt-cm and photoconductivity can be observed, although chalcopyrite contains transition element, Fe, as a constituent element.

The crystal structure of chalcopyrite is a substitutional analogue of that of diamond. (Fig. 8). Therefore all atoms are tetrahedrally sited in the lattice. In this material all atoms will form covalent $sp^3$ bonds when copper atom contributes one electron and iron three electrons to the covalent bond. According to this model five unpaired electrons should remain in the d-shell of iron. At all events the d-shell will be independent of the valence $sp^3$ bond.

The energy band gap obtained from the temperature dependence of conductivity in the intrinsic range is about 2.6 eV. This value is far large compared with that obtained by other authors[4)5)].

According to the phase diagram of Cu-Fe-S system[9)] chalcopyrite phase region extends to metal rich side. (Fig. 9). This will be the reason why the conduction of chalcopyrite is of N-type, since it is well known that some compounds, for example, lead sulphide and zinc sulphide, have an N-type conduction[10)] when these compounds contain excess metal atoms.

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## DISCUSSION

S. MIYAHARA: Could you find any trace of decomposed material at high temperatures by X-ray or other devices?

T. TERANISHI: Yes, we found a certain amount of sulphur adhered on the wall of the silica capsule after we quenched the capsule containing the specimen from about 900°C.