

# Delocalization of d electrons in the $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$ system

T Teranishi<sup>†</sup>, K Sato<sup>†</sup> and Y Saito<sup>‡</sup>

<sup>†</sup>Broadcasting Science Research Laboratories of Nippon Hoso Kyokai, Kinuta, Setagaya, Tokyo 157, Japan

<sup>‡</sup>Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku, Tokyo 162, Japan

**Abstract.** The magnetic susceptibility, electrical conductivity and optical reflectance of a  $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$  system have been measured as functions of the magnetic ion concentration. The paramagnetic moment obtained from the magnetic susceptibility and the activation energy of electrical conduction decrease suddenly above the magnetic ion concentration  $x \approx 0.12$ . Reflectivities of specimens with  $x \geq 0.1$  are far larger than those with  $x \leq 0.07$ .

Abrupt changes of these properties at  $x \approx 0.1$  are understood by the delocalization of d electrons originating in p/d mixing and by the formation of energy band. Moreover, it is suggested that small values of the critical concentration  $x \approx 0.1$  results from the strong covalency of chalcopyrite-type compounds.

## 1. Introduction

It has been known that magnetic ions bring about unfavourable effects on chalcopyrite-type semiconductors; for example, iron impurities make the crystal opaque. This is caused by a strong charge-transfer-type transition from p-states of anions to d-states of iron impurities (Schneider 1973, Teranishi *et al* 1974, Kambara 1974).

The same magnetic ion, however, gives some interesting properties to these semiconductors; the problems of delocalization of d-electrons. In the extreme case of high magnetic ion concentration, that is, in  $\text{CuFeS}_2$  the unoccupied 3d orbitals of iron ions are considerably hybridized with p orbitals of anions and the fraction of p in the hybridized orbitals is about 50% (Kambara 1974). Owing to this large hybridization, the unoccupied d states are extended over the neighbouring iron ions and energies of these states form a conduction band.

A similar circumstance is also realized in the valence band; d orbitals occupied by electrons with opposite spin mix into the valence band states. This hybridization gives rise to a reduction of iron magnetic moment from the value expected for trivalent iron ions. A small magnetic moment,  $3.85 \mu_B$ , observed in  $\text{CuFeS}_2$  by neutron diffraction (Donnay *et al* 1958) is attributed to this hybridization.

On the other hand, in the case of very small concentrations of magnetic ion d orbitals of iron behave like those of the localized electron. Photoluminescence of  $\text{CuAlS}_2:\text{Fe}$  and  $\text{CuGaS}_2:\text{Fe}$  (Sato and Teranishi 1974) and ESR spectrum of  $\text{CuGaS}_2:\text{Fe}$  (Schneider

*et al* 1973) have been explained by a spin multiplicity expected for the multiplet  ${}^6A_1$  of the localized many-electron system. Within a cluster consisting of a central magnetic ion and its nearest-neighbour anions, the real wavefunction of a d electron is more or less mixed with that of a p-electron, but the spin multiplicity of the whole cluster remains unchanged (Kambara *et al* 1975). This means that the mixing of p orbitals into d orbitals is limited within the cluster, so that d orbitals are not spread over the crystal.

When the concentration of the magnetic ion is increased and exceeds a critical value, the p/d mixing should increase, and the previously localized d electron becomes delocalized to form an energy band. This delocalization of the d electron makes the property of the Fe-doped crystal similar to that of the magnetic semiconductor,  $\text{CuFeS}_2$ .

The purpose of the present paper is to determine the concentration of magnetic ions at which the delocalization of the d electron occurs, from measurements of magnetic susceptibility, electrical conductivity and optical reflectance on the  $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$  system.

All of these properties show an abrupt change at the value  $x \approx 0.1$ , above which d electrons are considered to be delocalized. Furthermore, the origin of this rather small value of critical concentration is discussed.

## 2. Experimental

### 2.1. Specimen

Single crystals of the  $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$  system were grown by means of chemical transport reaction. The concentration of iron ions in the single crystals thus obtained may differ from the nominal value, since sometimes they exhibit various colours depending on their locations in the reaction tube.

Sintered powder samples were used for magnetic and electrical measurements because they are considered to have appropriate concentrations of magnetic ions.

For the reflectance measurements, crystals with smooth and clean surfaces are required. Efforts to grow crystals from the melt were not successful, although the substance could be melted at about  $1250^\circ\text{C}$ , specimens were not obtained because they reacted with the silica reaction tube and were oxidized. Single crystals grown by chemical transport reaction were used for the reflectance measurements, although some ambiguities were inevitable as for the concentration of magnetic ions.

### 2.2. Magnetic susceptibility

In order to study the concentration dependence of the paramagnetic moment, the magnetic susceptibility as a function of temperature was measured with a magnetic balance from liquid-nitrogen temperature up to 700 K, then the Curie constant was determined. For this purpose it is desirable to measure the susceptibility up to temperatures as high as possible, but the decomposition of specimens may occur at high temperatures.

After the measurement up to 700 K the heater was removed and the sample was cooled to room temperature, when the susceptibility was again measured. Differences in the values of susceptibility of all specimens before and after the heating to 700 K were within 1.5%. DiGiuseppe *et al* (1974) measured the magnetic susceptibility and

Mössbauer effect of  $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$  system up to 650 K and have not found any indication of decomposition. These facts show that the decomposition of specimens is negligibly small even at 700 K.

### 2.3. Electrical conductivity

The electrical conductivity of a sintered powder specimen of the  $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$  system was measured between room temperature and liquid-nitrogen temperature by the four-electrode method. The ohmic contact of electrodes was provided by Du Pont 4817 silver paste.

### 2.4. Optical reflectivity

Optical-reflection measurements were carried out at room temperature on single crystals grown by chemical transport reaction. A light beam from a monochromator was divided into two beams by a half mirror. One beam was chopped at 35 Hz and reflected by the specimen, and the other was chopped at 320 Hz and reflected by a standard mirror, Ag or Al. Both were led into a single detector, and each component of output of the detector was amplified by an amplifier tuned to each frequency. In this way, reflectivity was measured directly as a ratio of reflected light from the specimen to that from the standard mirror.

## 3. Results and discussion

### 3.1. Magnetic susceptibility

The temperature dependence of inverse molar susceptibility  $1/\chi_M$  is given in figure 1. For specimens of low iron concentration  $1/\chi_M$  changes linearly with temperature. Specimens with  $x < 0.12$  have paramagnetic moments of about  $6\mu_B$ , which correspond to the value of the localized iron ion,  $S = 5/2$ . For specimens with higher iron concentration the linearity of  $1/\chi_M$  with temperature does not hold at low temperatures. However,

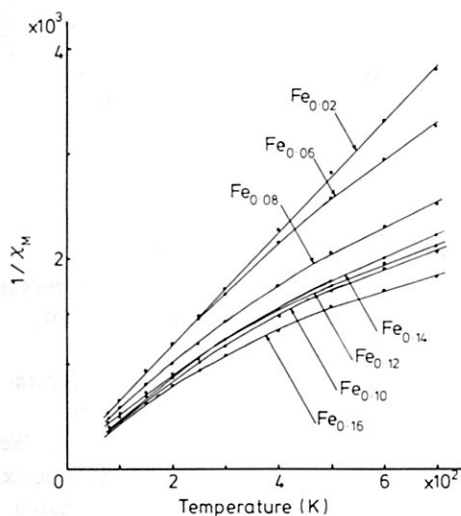


Figure 1. Temperature dependences of inverse molar susceptibility of the  $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$  system.

above 400 K the inverse susceptibility follows Curie–Weiss law. The obtained paramagnetic moment is about  $5 \mu_B$  for compositions with  $x > 0.12$ .

In figure 2(a) paramagnetic moments thus obtained are plotted against iron concentration  $x$ . It is remarkable that there occurs an abrupt reduction of paramagnetic moment by  $1 \mu_B$  at  $x = 0.12$ .

Kambara (1974) have calculated energies and wavefunctions of molecular orbitals in the iron-containing cluster in  $\text{CuGaS}_2\text{:Fe}$  and  $\text{CuFeS}_2$ . In  $\text{CuFeS}_2$  occupied 3d orbitals with opposite spin mix into valence band states and the electron population was  $(3d\uparrow)^{4.8}(3d\downarrow)^{2.0}$  for the centre iron and  $(3d\downarrow)^{5.0}(3d\uparrow)^{1.3}$  for the corner iron of the cluster. From this electron population the spin polarization is obtained as  $2.8 \mu_B$  for the centre iron and as  $-3.7 \mu_B$  for the corner iron. These values are close to that measured by neutron diffraction experiment,  $3.85 \mu_B$  (Donnay *et al* 1958).

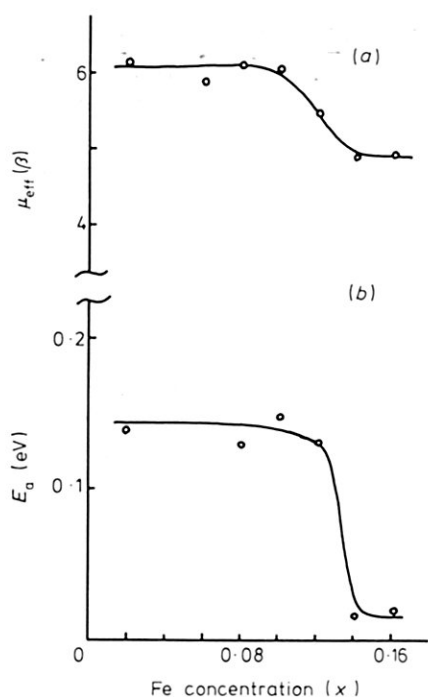


Figure 2. Magnetic ion concentration dependences of (a) paramagnetic moment and (b) activation energy of electrical conductivity.

The abrupt reduction, at  $x = 0.12$ , of the paramagnetic moment from that of a localized iron suggests that the delocalization of 3d orbitals takes place due to the mixing of 3d orbitals with opposite spin into the valence band, though the reduced moment,  $5 \mu_B$ , seems somewhat larger than the calculated value mentioned above.

As previously mentioned, inverse susceptibilities of specimens with a high concentration of iron ions deviate from the Curie–Weiss behaviour at low temperatures. The formation of iron ion clusters (pairs, triads, etc) may give the origin of this deviation. We calculated susceptibilities by a model based on iron pairs, using the antiferromagnetic exchange interaction ranging from  $10 \text{ cm}^{-1}$  to  $1000 \text{ cm}^{-1}$ . The deviation of the calculated

susceptibility from Curie–Weiss law was not large enough to explain the observed susceptibility by this model.

Another probable origin of the deviation from Curie–Weiss law is Pauli spin paramagnetism. We proposed previously that the temperature-independent susceptibility of  $\text{CuFeS}_2$  is understood by Pauli spin paramagnetism if  $\text{CuFeS}_2$  is assumed to be a degenerate semiconductor (Teranishi and Sato 1975). When the number  $n$  of electrons in the energy band is not large, the degeneracy lifted up and the Fermi distribution function can be approximated by the Boltzmann distribution function. This gives the susceptibility  $\chi_M = (n \mu_B^2)/kT$ , which has just the same form with the Curie–Weiss law. In this case it should be noted that the slope of  $1/\chi_M$  against temperature curve does not express the localized magnetic moment, but the number of electrons in the energy band,  $n$ . As mentioned above, it is suggested that 3d electrons are delocalized and the energy band is formed in the  $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$  with  $x > 0.12$ . It is then quite probable that

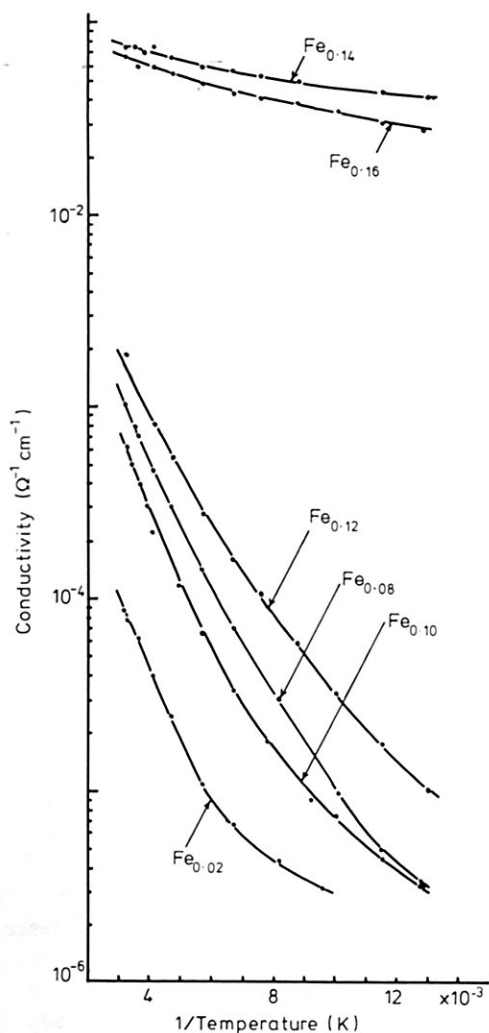


Figure 3. Temperature dependences of electrical conductivity of the  $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$  system.

the susceptibilities of these compounds are explained by Pauli paramagnetism with small electron numbers. In that case, susceptibilities should show the temperature dependence just like the observed susceptibility (figure 1), if the electron number in the energy band is not enough for the Fermi distribution, and changes with temperature.

### 3.2. Electrical conductivity

Figure 3 shows the temperature dependences of electrical conductivity in the  $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$  system. It is seen from figure 3 that all the specimens are semiconductive and that specimens with  $x < 0.12$  have low conductivity and large activation energy, while specimens with  $x \geq 0.14$  have considerably larger conductivity and smaller activation energy. In figure 2(b) plots of activation energy against iron ion concentration  $x$  are shown. There is also an abrupt reduction of activation energy at  $x = 0.12$ .

From these results it is considered that the electrical conduction arises mainly from the hopping conduction in the very narrow d band. Over the critical concentration  $x = 0.12$  of iron ions, the mixing of p orbitals into unoccupied d states increases abruptly, and the conduction band is formed. The reason why the activation energy decreases suddenly at this critical concentration can therefore be explained.

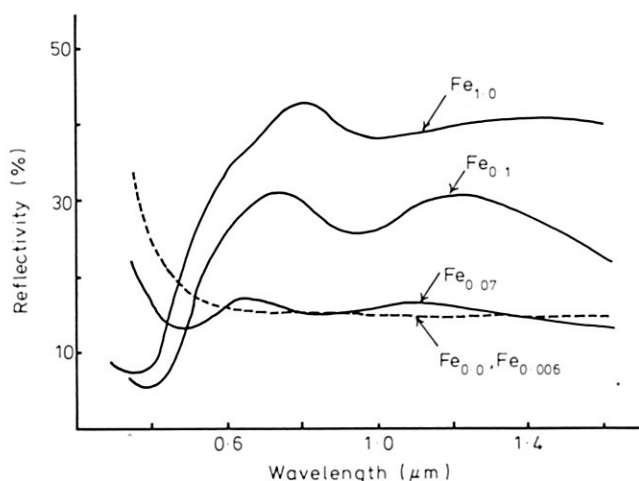


Figure 4. Reflectivity spectra of the  $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$  system.

### 3.3. Optical reflection

Reflection spectra of five specimens grown by chemical transport reaction are shown in figure 4. It should be noted that the reflectivities of compositions with  $x = 1.0$  and  $0.1$  are far larger than those with  $x \leq 0.07$  for wavelengths longer than  $0.5 \mu\text{m}$ .

Those two specimens with higher iron concentration have a metallic lustre, while specimens with  $x \leq 0.07$  have no lustre; this is presumably caused by the large difference in the observed reflectivity.

When a material has a wide conduction band and accordingly has large DC conductivity, large reflectivity of Hagen-Rubens type should be expected in the infrared

region, the tail of which may extend over the visible region. It is therefore considered that the large reflectivity in compositions with  $x = 0.1$  also gives proof of the formation of a wide conduction band originating from the mixing state of 3d and p orbitals.

For a more precise discussion it is necessary to obtain spectra of refractive index  $n$  and extinction coefficient  $k$ , which are obtained from reflection spectra from Kramers–Krönig analysis. Because of the limited spectral range of the observation, we cannot apply accurate Kramers–Krönig transformation, although we can give a brief discussion about the golden lustre of specimens with  $x \geq 0.1$ .

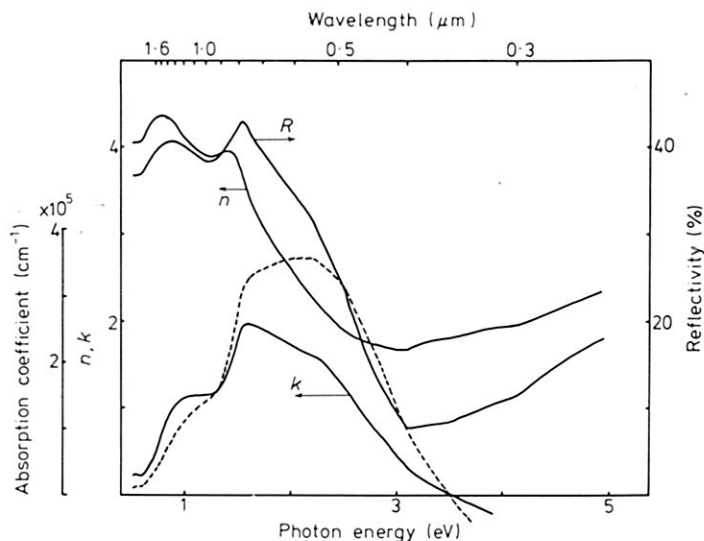


Figure 5. Spectra of reflectivity ( $R$ ), optical constants  $n$  and  $k$ , and absorption coefficient of  $\text{CuFeS}_2$  (broken line).

The reflectivity spectra of these specimens have a broad peak at about  $0.8 \mu\text{m}$  ( $1.6 \text{ eV}$ ). In figure 5 are shown spectra of  $n$  and  $k$  for  $\text{CuFeS}_2$  ( $x = 1.0$ ) obtained from the reflectivity spectra by Kramers–Krönig analysis. From the spectrum of absorption coefficient  $2\omega k/c$ , it is clear that the peak of absorption coefficient at  $2 \text{ eV}$  corresponds to the peak of reflectivity at  $0.8 \mu\text{m}$ . This absorption peak thus obtained corresponds to that observed by us at  $2 \text{ eV}$  on a very thin film of  $\text{CuFeS}_2$  (Sato and Teranishi 1976). This absorption peak is the origin of the golden lustre of chalcopyrite.

$\text{CuAl}_{0.9}\text{Fe}_{0.1}\text{S}_2$  has the same reflectivity spectrum as that of  $\text{CuFeS}_2$  and also has a golden lustre.

#### 4. Conclusion

In the present work on magnetic susceptibility, electrical conductivity and optical reflectivity it should be noted that these properties change very critically at about  $0.1$  of magnetic ion concentration  $x$ . These phenomena give proof that with the increase in iron ion concentration, the hybridization of anion p orbitals and magnetic ion 3d orbitals grows larger, the delocalization of d electrons takes place and the energy band is formed.

Moreover, it is remarkable that the value of the critical concentration  $x \approx 0.1$  to form the energy band is very small. This means that the band formation is not based on the direct overlap of d orbitals but on the p/d mixing which comes from the strong covalency of chalcopyrite-type compounds. The abrupt change of d-electrons from localized to delocalized states reminds us of the Mott metal-insulator transition.

As our observation was rather limited to a qualitative one, more quantitative measurement on well prepared specimens are required for a more detailed discussion.

### References

- DiGiuseppe M, Steger J, Wold A and Kostiner E 1974 *Inorg. Chem.* **13** 1828-31  
Donnay G, Corliss L M, Donnay J D H, Elliott N and Hastings J M 1958 *Phys. Rev.* **112** 1917-23  
Kambara T 1974 *J. Phys. Soc. Japan* **36** 1625-35  
Kambara T, Suzuki K and Gondaira K I 1975 *J. Phys. Soc. Japan* **39** 764-71  
Schneider J, R uber A and Brandt G 1973 *J. Phys. Chem. Solids* **34** 443-50  
Sato K and Teranishi T 1974 *J. Phys. Soc. Japan* **37** 415-22  
— 1976 *J. Phys. Soc. Japan* **40** 297-8  
Teranishi T and Sato K 1975 *J. Physique* **36** C3 149-53  
Teranishi T, Sato K and Kondo K 1974 *J. Phys. Soc. Japan* **36** 1618-24