

OPTICAL, ELECTRICAL AND MAGNETIC PROPERTIES OF CHALCOPYRITE, CuFeS₂

T. Teranishi, K. Sato

► To cite this version:

T. Teranishi, K. Sato. OPTICAL, ELECTRICAL AND MAGNETIC PROPERTIES OF CHALCOPYRITE, CuFeS₂. Journal de Physique Colloques, 1975, 36 (C3), pp.C3-149-C3-153. <10.1051/jphyscol:1975327>. <jpa-00216297>

HAL Id: jpa-00216297

<https://hal.archives-ouvertes.fr/jpa-00216297>

Submitted on 1 Jan 1975

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

OPTICAL, ELECTRICAL AND MAGNETIC PROPERTIES OF CHALCOPYRITE, CuFeS_2

T. TERANISHI and K. SATO

Broadcasting Science Research Laboratories of Nippon Hoso Kyokai
Setagaya, Tokyo 157, Japan

Résumé. — Diverses propriétés optiques, électriques et magnétiques du semiconducteur magnétique CuFeS_2 ont été étudiées. Les spectres optiques montrent que le bord d'absorption se situe à 0,6 eV pour CuFeS_2 alors que de fortes bandes d'absorption apparaissent à 1,3 et 2,0 eV pour CuAlS_2 dopé au Fe. La photoconductivité a été observée dans la même région spectrale. Ces fortes absorptions ont pour origine des transitions de transfert de charge en relation avec les orbitales 3d du Fe, et le bord d'absorption de CuFeS_2 résulte de transitions bande à bande correspondant à ces transitions de transfert de charge. Pour CuFeS_2 de types n et p, la conductivité électrique augmente légèrement quand la température décroît et la concentration des porteurs est indépendante de la température. Les valeurs des mobilités sont faibles : $10 \text{ cm}^2/\text{V} \cdot \text{s}$ pour le type n et $1 \text{ cm}^2/\text{V} \cdot \text{s}$ pour le type p. La susceptibilité magnétique est indépendante de la température entre 40 et 600 K et elle est d'environ 10^{-3} par mole.

Ce comportement métallique apparent des propriétés électriques et magnétiques se comprend à partir d'un modèle de semiconducteur dégénéré où les orbitales 3d fortement hybridées aux orbitales s et p constituent les bandes de valence et de conduction.

Abstract. — Various optical, electrical and magnetic properties of a magnetic semiconductor, CuFeS_2 , have been studied. Optical absorption spectra show the absorption edge at 0.6 eV for CuFeS_2 and strong absorption bands at 1.3 eV and 2.0 eV for Fe-doped CuAlS_2 . Photoconductivity is also observed at the same energy region of the absorption edge. These strong absorptions originate from the charge transfer transitions relating to 3d orbitals of Fe and the absorption edge of CuFeS_2 rises from the band-to-band transition corresponding to this charge transfer transition. For n- and p-type CuFeS_2 electrical conductivities increase slightly with decreasing temperature and carrier concentrations do not depend on temperature. Mobility has small value as $10 \text{ cm}^2/\text{V} \cdot \text{s}$ for n-type specimen and $1 \text{ cm}^2/\text{V} \cdot \text{s}$ for p-type. Magnetic susceptibility is also temperature independent between 40 K and 600 K and its magnitude is 10^{-3} per mol.

These apparent metallic behaviors of electric and magnetic properties are understood from a model of a degenerate semiconductor where 3d orbitals are appreciably admixed with s and p orbitals and compose both the conduction and valence band.

1. Introduction. — Chalcopyrite, CuFeS_2 , is the only one magnetic semiconductor among the chalcopyrite type ternary semiconducting compounds. Electrical [1, 2], magnetic [3, 2], and optical [4, 5] properties of chalcopyrite have been examined by some investigators. The results of these investigations have been interpreted from a standpoint of an ordinary non magnetic semiconductor or a simple magnetic material. But some experimental results, for instance, the low mobility of n-type chalcopyrite [2], the small value of effective magnetic moment obtained by neutron diffraction experiment [3], the extraordinarily high Néel temperature [2] and the low optical absorption edge [4, 5] are not understood from a model of a simple semiconductor or a magnetic material. It is possible to interpret these anomalous values by a conception of the magnetic semiconductor.

Recently we have observed the optical absorption of CuFeS_2 , and Fe-doped CuAlS_2 and CuGaS_2 [6]. It has been clarified that the transition from the valence

band to the 3d states causes the strong absorption. Theoretical calculations based on the molecular orbital method have revealed the nature of this transition quantitatively [7].

Still most of the above mentioned difficulties have remained abstruse.

The present work was undertaken to study the role of 3d orbitals in optical, electrical and magnetic properties, and to find a clue to solve the above mentioned difficulties.

We were able to make p-type specimens of chalcopyrite as well as n-type ones. In the present paper are described the results of electrical and magnetic measurements on specimens of both types, including the optical data published by us before [6].

2. Experimental. — 2.1. — A thin evaporated film of CuFeS_2 was used for the optical measurement. As for Fe-doped CuAlS_2 and CuGaS_2 we used single crystals which were grown as blades by the chemical

transport reaction. The details of the growing procedures of the film and crystals were described in a previous paper [6].

For the electrical measurement a bulky single crystal of CuFeS_2 was grown by the direct melting method. Powder of CuFeS_2 was put in the silica crucible, the tip of which was sharply pointed, and the crucible was suspended in the growing furnace. The temperature of the furnace was lowered at a rate of $2^\circ\text{C}/\text{hour}$ or the crucible was lowered at a rate of $20\text{ mm}/\text{day}$. This lowering rate was similar to that used by Adams *et al.* [8].

Because the most probable ionic state of chalcopyrite is $\text{Cu}^+\text{Fe}^{3+}\text{S}_2^{2-}$ it is possible to make a p-type specimen by reducing the valency of cations or by increasing the valency of anions. We have succeeded in preparing a p-type specimen of chalcopyrite by three ways: 1) the substitution of Zn^{2+} ions for Fe^{3+} , $\text{CuFe}_{1-x}\text{Zn}_x\text{S}_2$, 2) the substitution of Cu^{1+} ions for Fe^{3+} , $\text{Cu}_{1+x}\text{Fe}_{1-x}\text{S}_2$, 3) the substitution of Sb^{3-} ions for S^{2-} , $\text{CuFeS}_{2-x}\text{Sb}_x$. Sintered polycrystalline specimens of all these p-type compounds were prepared by the direct combination of elements.

An attempt to make a p-type single crystal by the chemical transport reaction was successful only for the series of $\text{CuFe}_{1-x}\text{Zn}_x\text{S}_2$. All single crystals grown by direct melting of these substituted powder specimens were not of p-type but n-type. Because a small amount of yellow elemental sulfur was sometimes noticed on the surface of the crystal boule, it is supposed that the cause of forming the n-type crystals is the deficiency of sulfur in the crystal.

All samples were analysed by x-ray diffraction techniques and ascertained that phases other than chalcopyrite were not present.

2.2 OPTICAL MEASUREMENTS. — Optical absorption measurements were made with a Cary 14 spectrophotometer. In the range of wave length beyond $2\ \mu\text{m}$ a single beam infrared spectrometer was used.

2.3 ELECTRICAL MEASUREMENTS. — The electrical conductivity and the Hall effect were measured by five electrode method. The contact of electrodes to the specimen was made with an In amalgam.

For p-type specimens except one which was introduced by Zn^{2+} ions the measurement was made on sintered polycrystalline samples at room temperature.

2.4 MAGNETIC MEASUREMENTS. — Magnetic susceptibility data were obtained using a Faraday balance. The correction for diamagnetism was performed on the basis of molar diamagnetic susceptibilities given by Selwood [9].

3. Results and Discussion. — **3.1 OPTICAL ABSORPTION.** — The evaporated thin film of CuFeS_2 shows a strong absorption rising at $0.6\ \text{eV}$ as shown in figure 1 (curve a). This is regarded as the absorption edge of chalcopyrite by Austin *et al* [5]. The Fe-doped

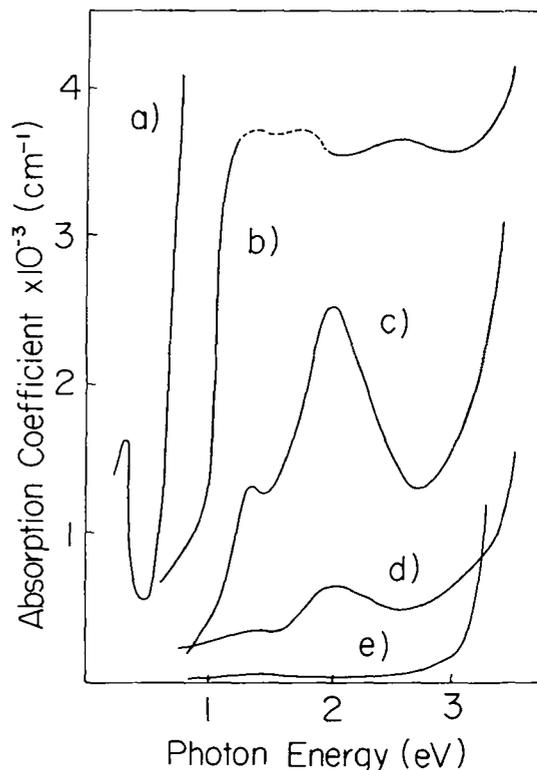


Fig. 1 — Absorption spectra of a) CuFeS_2 , b) $\text{CuAl}_{0.93}\text{Fe}_{0.07}\text{S}_2$, c) $\text{CuAl}_{0.994}\text{Fe}_{0.006}\text{S}_2$, d) $\text{CuAl}_{0.9992}\text{Fe}_{0.0008}\text{S}_2$, and e) CuAlS_2 .

CuAlS_2 crystals show the strong absorption band at $1.3\ \text{eV}$ and $2.0\ \text{eV}$ besides the fundamental absorption edge rising at $3.3\ \text{eV}$ (Fig. 1, curve b, c and d). The intensity of these absorption increases with the amount of doped Fe ions and grows into the absorption edge of CuFeS_2 . The similar results are obtained for $\text{CuGaS}_2 : \text{Fe}$ [6].

It is naturally expected that 3d electrons take part in this absorption. Since the estimated oscillator strength is as large as 7×10^{-2} , it is indicated that this large absorption does not result from a typical d-d transition of isolated magnetic ions but from a charge transfer transition between the valence band and the empty 3d states. Moreover, at liquid nitrogen temperature the photoconductivity is observed on a natural single crystal of CuFeS_2 just at the energy region where the absorption edge is also located (Fig. 2). It is, therefore, concluded that the empty 3d states form the conduction band mixed by s and p orbitals of sulfur and the above mentioned charge transfer transition can be regarded as a band-to-band transition.

Shay *et al.* have reported that the highest valence band of I-III-VI₂ compounds results from a hybridization of the Cu 3d orbitals with p orbitals on the other atoms [10]. As for CuFeS_2 the filled Fe 3d orbitals as well as Cu 3d ones are expected to contribute appreciably to the highest valence band.

Consequently it is believed that both conduction and valence band of CuFeS_2 are indeed narrow, because they are derived from the hybridized states

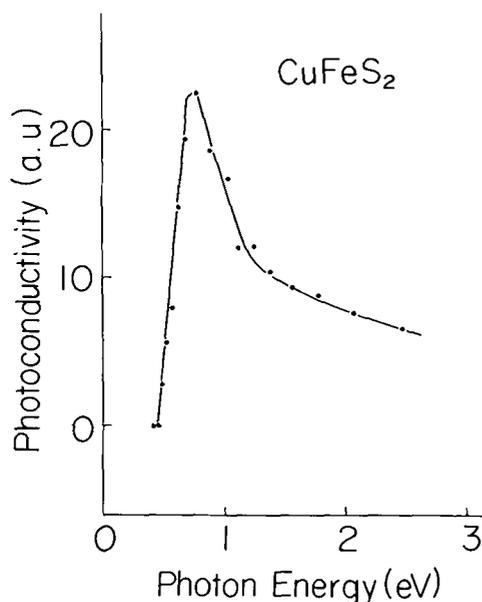


FIG. 2. — Photoconductivity spectrum of CuFeS_2 at liquid nitrogen temperature.

of the d orbitals with p and s orbitals. This will be supported by observing the mobility of electrons and holes.

Another evidence of the strong hybridization of 3d orbitals with s and p orbitals is the low energy of luminescence lines of Fe^{3+} . We have observed a sharp luminescence line at 0.72 eV for $\text{CuAlS}_2 : \text{Fe}$ and at 0.61 eV for $\text{CuGaS}_2 : \text{Fe}$ [11]. Though the nature of transition is clarified from the observation of Zeeman effect, the pretty low energy of these emission lines is not explained in terms of the usual d-d transition. It is theoretically explained on the basis of the 3d states hybridized with s and p orbitals by taking account of configuration interaction [12].

3.2 ELECTRICAL CONDUCTIVITY AND HALL EFFECT. —

Electrical measurements were carried out on two samples: a) n-type single crystal which was grown by the direct melting method and b) p-type single crystal which contained 0.1 atomic % of Zn ions in nominal concentration and was made by the chemical transport method. Figure 3 shows plots of conductivity vs. temperature from room temperature to liquid nitrogen temperature. In this temperature range conductivities of both n- and p-type crystals decrease with the rising temperature.

Hall effect is also measured in the same temperature range and the sign of carriers is the same with that determined from the thermoelectric power. In figure 4 we show the temperature variation of carrier concentration estimated from the Hall coefficient on the basis of the simple one band model. Carrier concentrations are rather large for both crystals and have no temperature dependence.

Hall mobilities estimated from the same simple model are given in figure 5. The mobility of the n-type

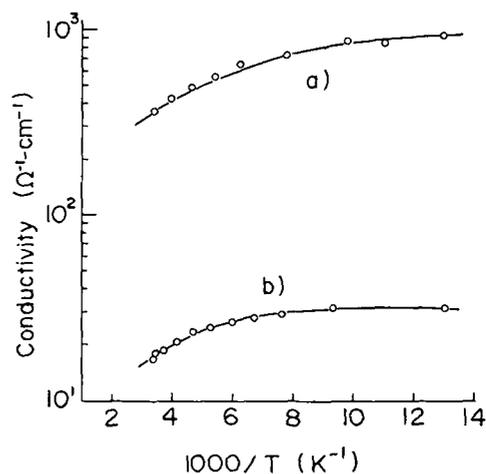


FIG. 3. — Temperature dependence of conductivity in a) n-type CuFeS_2 , and b) p-type $\text{CuFe}_{0.9}\text{Zn}_{0.1}\text{S}_2$.

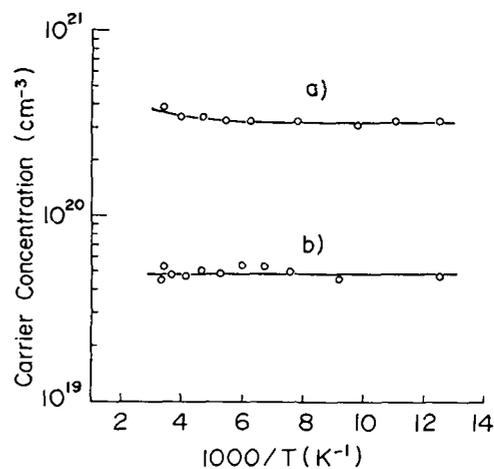


FIG. 4. — Temperature dependence of carrier concentration in a) n-type CuFeS_2 , b) p-type $\text{CuFe}_{0.9}\text{Zn}_{0.1}\text{S}_2$.

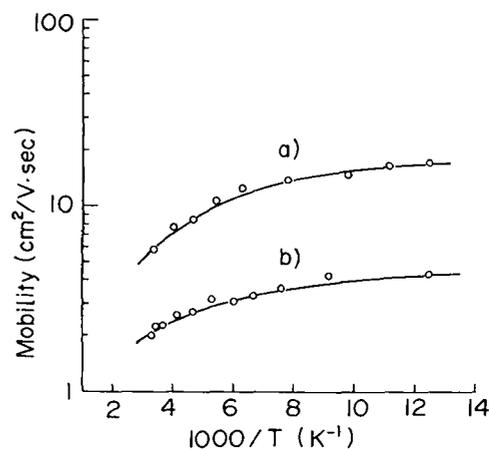


FIG. 5. — Temperature dependence of mobility in a) n-type CuFeS_2 and b) p-type $\text{CuFe}_{0.9}\text{Zn}_{0.1}\text{S}_2$.

synthetic single crystal is $10 \text{ cm}^2/\text{V}\cdot\text{s}$, being the same order of magnitude with that of a natural n-type single crystal [2]. The mobility of p-type crystal is an

order of magnitude less than that of the n-type crystal.

Electrical properties are also measured on p-type sintered polycrystalline specimens at room temperature alone. The results are summarized in table I. The magnitude of mobility of these p-type specimens is the same order or a little smaller than that of a single crystal.

It should be noticed here that the mobility of chalcopyrite is pretty small for both n- and p-type crystals compared with an usual semiconductor which contains no magnetic ions. This indicates that the state density is large at the bottom of the conduction band and at the top of the valence band because these bands are composed of 3d orbitals hybridized with s and p orbitals.

The temperature dependence of the conductivity and the temperature independent carrier concentration give evidence that this material have a metallic behavior rather than semiconducting. This is also supported by the result of magnetic susceptibility measurement as seen in a later section.

It seems natural to interpret that this metallic behavior results from the *degenerate* semiconducting state of chalcopyrite at room temperature. Under this condition we have attempted to obtain an estimate of the effective mass, m^* , of the carrier using [13]:

$$T_d = (3n/\pi)^{2/3} (h^2/8km^*),$$

where T_d is the degenerate temperature, n is the carrier concentration. For T_d we have used the room temperature, 300 K, and for n we have used $3.5 \times 10^{20}/\text{cm}^3$ for n-type CuFeS_2 single crystal. The ratio of the effective mass to the free electron mass determined in this way is 4.2. This large value is not unnatural when the small mobility of this material is taken into account.

3.3 MAGNETIC SUSCEPTIBILITY. — The temperature dependence of the magnetic susceptibility is shown in figure 6 for three specimens: a) n-type natural crystal, b) n-type synthetic crystal, and c) p-type $\text{Cu}_{1.1}\text{Fe}_{0.9}\text{S}_2$.

It is remarkable that the magnetic susceptibilities of all specimens do not depend on temperature in the range between 40 K and 600 K and its amount, 10^{-3} per mol, is rather large. DiGiuseppe *et al.* have also found the temperature independent susceptibility of chalcopyrite [14], but they do not refer to its origin. The sudden increase of the susceptibility below 40 K

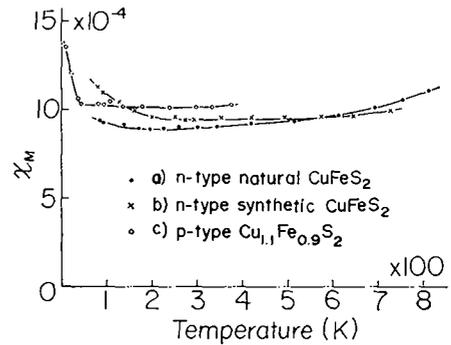


FIG. 6. — Temperature dependence of magnetic susceptibility of natural CuFeS_2 , synthetic CuFeS_2 , and $\text{Cu}_{1.1}\text{Fe}_{0.9}\text{S}_2$.

for $\text{Cu}_{1.1}\text{Fe}_{0.9}\text{S}_2$ and the slight temperature dependence in a low temperature range for the synthetic crystal may be the result of a small amount of the paramagnetic impurity, e. g. FeS , which is formed during the synthetic processes. The increasing of the susceptibility above 600 K is probably owing to the decomposition of specimens.

Eventually it is evident that the temperature independence of the magnetic susceptibility is the specific property of chalcopyrite; it indicates that the susceptibility does not follow the Curie-Weiss law and electrons participating in the magnetism are more or less delocalized. As the origin of this constant susceptibility we assume the Pauli spin paramagnetism although some experimental results are unfavorable for the model: the neutron diffraction experiment shows that chalcopyrite is antiferromagnetic, and the rectifying property [1] and the large thermoelectric power [2] show chalcopyrite is not metallic but semiconducting. On the other hand the magnetic moment, $3.85 \mu_B$, observed by a neutron diffraction is far less than $5 \mu_B$ to be expected for localized trivalent irons [3]. Moreover, the results of Hall effect suggest the p- and n-type chalcopyrite are degenerate semiconductors as shown in a previous section. These facts imply the delocalization of d electrons and the apparent metallic behavior, supporting the application of the Pauli spin paramagnetism.

The theoretical calculation of the electronic structure has been carried out in the framework of the molecular orbital method and has led to the conclusion that the unoccupied 3d orbitals are delocalized making the

TABLE I

Conductivity, carrier concentration and mobility of p-type polycrystalline specimens at room temperature

Substance	Conductivity ($\text{ohm}^{-1} \text{cm}^{-1}$)	Carrier concentration (cm^{-3})	Mobility ($\text{cm}^2/\text{V} \cdot \text{s}$)
$\text{CuFe}_{0.95}\text{Zn}_{0.05}\text{S}_2$	3.5	4.5×10^{19}	0.5
$\text{CuFe}_{0.9}\text{Zn}_{0.1}\text{S}_2$	0.4	0.2×10^{19}	1.4
$\text{Cu}_{1.05}\text{Fe}_{0.95}\text{S}_2$	3.9	1.8×10^{19}	1.3
$\text{CuFeS}_{1.9}\text{Sb}_{0.1}$	16.9	3.1×10^{20}	0.3

conduction band while the occupied states are localized in the valence band [7].

At present it is impossible to identify where the Fermi level lies. But the large and temperature independent susceptibility results when the Fermi level situates at the bottom of the conduction band or at the top of the valence band, both of which are composed of 3d orbitals admixed with s and p orbitals. On the basis of the model of Pauli spin paramagnetism the molar susceptibility χ_M is given by [15]:

$$\chi_M = 2 \mu_B^2 N(E_f) \cdot N_A \cdot 6.242 \times 10^{11},$$

where $N(E_f)$ is the state density per magnetic ion per eV at the Fermi energy, E_f , and μ_B is Bohr magneton, and N_A is Avogadro number. Using the observed molar susceptibility $\chi_M = 10^{-3}$ we estimate the state density $N(E_f)$ at 16/ion. eV. This value is reasonable, considering the similar value, 15/ion. eV, obtained from the temperature independent part of the magnetic susceptibility of V₂O₃ [16], in which the relevant energy band is composed of 3d orbitals.

4. Conclusion. — From a standpoint of a magnetic semiconductor we have studied properties of CuFeS₂,

extending and improving the measurements of optical, electrical and magnetic properties. Though many of the studies have been hampered by poorly characterized specimens most of anomalous properties pointed out at section 1 are understood on the basis of delocalized 3d orbitals which admix appreciably with s and p orbitals and compose both the conduction and valence band.

But the interpretation of the temperature independent susceptibility as due to the Pauli spin paramagnetism is still rather speculative, because a *degenerate* semiconductor is essentially an extrinsic semiconductor. Moreover it remains unexplained whether the coexisting of an antiferromagnetism and a metallic state is possible for CuFeS₂.

It is required to study more precisely the temperature dependence of the susceptibility on an extremely pure specimen of chalcopyrite with more carefully controlled impurity concentrations.

Acknowledgment. — We would like to thank Professors Kambara and Gondaira for helpful discussions. Our sincere thanks are also due to Mr. Tamaki for measurements of the magnetic susceptibility.

References

- [1] BOLTAKS, B. I. and TALNOVKII, N. N., *Zh. Tekh. Fiz.* **25** (1955) 402.
- [2] TERANISHI, T., *J. Phys. Soc. Japan* **16** (1961) 1881.
- [3] DONNAY, G., CORLISS, L. M., DONNAY, J. D. H., ELLIOTT, N. and HASTINGS, R. M., *Phys. Rev.* **112** (1958) 1917.
- [4] GOODMAN, C. H. L. and DOUGLAS, R. W., *Physica* **20** (1954) 1107.
- [5] AUSTIN, I. G., GOODMAN, C. H. L. and PENGELLY, A. E., *J. Electrochem. Soc.* **103** (1956) 609.
- [6] TERANISHI, T., SATO, K. and KONDO, K., *J. Phys. Soc. Japan* **36** (1974) 1618.
- [7] KAMBARA, T., *J. Phys. Soc. Japan* **36** (1974) 1625.
- [8] ADAMS, R., BEAULIEU, R., VASSILIADIS, M. and WOLD, A., *Mater. Res. Bull.* **7** (1972) 87.
- [9] SELWOOD, P., *Magnetochemistry* (Interscience, New York) 1956, p. 78.
- [10] SHAY, J. L., TELL, B., KASPER, H. M. and SHIAVONE, L. M., *Phys. Rev. B* **5** (1972) 5003.
- [11] SATO, K. and TERANISHI, T., *J. Phys. Soc. Japan* **37** (1974) 415.
- [12] KAMBARA, T., SUZUKI, K. and GONDAIRA, K., to be published in *J. Phys. Soc. Japan*.
- [13] SHOCKLEY, W., *Electrons and Holes in Semiconductors* (van Nostrand, New York) 1950, p. 283.
- [14] DIGIUSEPPE, M., STEAGER, J., WOLD, A. and KOSTINER, E., *Inorg. Chem.* **13** (1974) 1828.
- [15] WILSON, A. H., *The Theory of Metals* (University Press, Cambridge) 1953, p. 151.
- [16] KACHI, S., TAKADA, T., BANDO, Y., KOSUGE, K., OKINAKA, H. and NAGASAWA, K., *Proc. Int. Conf. Ferrite, Kyoto* (ed. by Hoshino, Iida and Sugimoto, Tokyo University Press) 1971, p. 563.