Optical Properties of a Magnetic Semiconductor: Chalcopyrite CuFeS₂.

I. Absorption Spectra of CuFeS₂ and Fe-Doped CuAlS₂ and CuGaS₂

Teruo Teranishi, Katsuaki Sato
and Ken'ichi Kondo*

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

(Received December 13, 1973)

Optical absorptions have been measured in chalcopyrite, CuFeS₂, and Fe-doped CuAlS₂ and CuGaS₂. An extra absorption band with two peaks is observed at the low energy region of the absorption edge for Fe-doped CuAlS₂ and CuGaS₂. Energy positions of two absorption peaks are 1.3 eV and 2.0 eV for CuAlS₂ and 1.2 eV and 1.9 eV for CuGaS₂, respectively. The intensity of this absorption band increases with the increase of doped Fe ions and grows into the absorption edge of CuFeS₂. Its oscillator strength comes up to $7 \cdot 10^{-2}$. In chalcopyrite photoconductivity is observed and its maximum is just at the same energy region of the absorption edge.

By comparing our results with those of absorption measurements for Cu- or Fe-doped ZnS it is concluded that this absorption band originates from the charge transfer transitions relating to 3d electron of Fe ions and the absorption edge of CuFeS₂ rises from the band-to-band transition corresponding to this charge transfer transition.

§ 1. Introduction

As the closest ternary analogues of the II-VI binary semiconductors many I-III-VI₂ compounds have been known.[1] Their crystal structure is derived from the zincblende structure in which two zinc ions are replaced orderly by a metal ion of group Ib and one of group IIIb. Recently a great deal of investigations has been reported on electrical and optical properties of I-III-VI₂ compounds since they are interesting semiconductors, showing nonlinear optical properties.[2-5]

Chalcopyrite, CuFeS₂, is the analogue of I-III-VI₂ semiconductors containing Ib metal and VI metalloid ions and having the same crystal structure with I-III-VI₂ semiconductors. Moreover, chalcopyrite is the only one compound which contains magnetic ions among these tetrahedrally coordinated semiconductors. (Some literature described the electrical and structural properties of AgFeTe₂ and CuFeSe₂. But the existence of these substances with chalcopyrite type structure is uncertain.[6]) It is naturally expected that chalcopyrite is a typical magnetic semiconductor.

The electrical properties of chalcopyrite show that this compound is a typical semiconductor. It has a rectifying property[7] and a large thermoelectric power.[8] According to the temperature dependence of electrical conductivity it seems that an intrinsic conduction occurs in the temperature range beyond 300°C where the activation energy is 1.3 eV.[5] So far as these electrical properties are measured there is no remarkable difference between chalcopyrite and the non-magnetic ordinary semiconductors. The value of Hall mobility of chalcopyrite is 35 cm²/volt-sec at liquid nitrogen temperature.[8] For a non-magnetic semiconductor this value is rather small and this smallness suggests some influence of the magnetic ion on the electrical conduction.

As to magnetic properties neutron diffraction[9] and static magnetic studies[8] have shown that chalcopyrite is an antiferromagnetics with the Néel temperature of 550°C. By neutron diffraction experiments effective magnetic moments of 3.85 μ_B and (0.0±0.2) μ_B were associated to the iron and copper atoms, respectively.[9]

---

* On leave from College of Science and Engineering, Aoyamagakuin University, Setagaya, Tokyo.

This small value of the effective magnetic moments of iron in chalcopyrite cannot be interpreted on the basis of the ionic state $Cu^+Fe^{3+}S_2$ which is expected from the similarity of valence states to those of I-III-VI$_2$ compounds.

Pauling and Brockway concluded that chalcopyrite is a mixture of two extreme ionic states $Cu^+Fe^{3+}S_2^{2-}$ and $Cu^{2+}Fe^{2+}S_2^{2-}$,[10] This mixed state is Pauling's expression of a rather covalent nature of chalcopyrite and the small magnetic moment of iron may result from this mixing.

On the other hand from Mössbauer studies it was shown that an iron ion was in the trivalent state in chalcopyrite.[11,12]

Unfortunately it is not yet able to obtain the information of the valence state of iron ions from the measurement of susceptibility because of its high Néel temperature and independence on temperature.

For I-III-VI$_2$ crystals in which Fe ions were very lightly doped Schneider *et al.* have observed the ESR spectra of trivalent irons.[13]

As for the optical properties Goodman and Austin *et al.* reported the result of the absorption measurements.[14,15] The absorption edge is at 0.5 eV and this value is much smaller than that of $CuGaS_2$ (2.5 eV).[2,8] If we put d-electrons aside the band gap of chalcopyrite would not be so different from that of $CuGaS_2$ which is the close analogue of $CuFeS_2$. Therefore, this low absorption edge of chalcopyrite suggests that this absorption is due to the transition relating to 3d electrons.

In order to clarify the origin of this low absorption edge and to get some informations of the ionic state of $CuFeS_2$ we performed optical measurements on the evapolated film of $CuFeS_2$ and single crystals of non-magnetic

analogues, $CuAlS_2$ and $CuGaS_2$, which are doped with the magnetic ion, Fe, in various concentrations. We report here the results of measurements of the optical absorption spectra.

At the low energy region of the absorption edge of non-magnetic Fe-doped crystals is observed an extra absorption band. The intensity of this new absorption band is very large and increases with the Fe ion concentration and eventually the absorption grows into the absorption edge of $CuFeS_2$. By comparing this absorption band with absorption spectra of Cu- or Fe-doped ZnS crystal and Fe-doped Ga_2S_3 crystal it is considered that the extra absorption in Fe-doped $CuAlS_2$ and $CuGaS_2$ originates from the charge transfer transition relating to Fe^{3+} ions and the absorption band edge of $CuFeS_2$ corresponds to this charge transfer transition. The theoretical foundation based on the molecular orbital model is discussed in the succeeding paper to support experimental results.

§ 2. Specimen Preparation

A thin film of chalcopyrite was obtained by the direct evapolation of chalcopyrite on the silica substrate. The thickness of the film determined from the amount of evaporated substance was $10\,\mu$ or less. The X-ray diffraction peaks were rather diffuse and the lattice constants are shown in Table I, compared with those of the natural chalcopyrite single crystal.

Single crystals of iron doped $CuAlS_2$ and $CuGaS_2$ were grown by the chemical transport reaction in the closed silica tube, using iodine as a transport agent. Cu_2S, FeS, Al (99.99 % pure) or Ga (99.99 %) and sulfur (99.99 %) were served as starting materials. Cu_2S and FeS powder were synthesized from Cu (99.99 %),

Table I. Lattice constants of chalcopyrite and chalcopyrite type compounds.

	ref.	a_0 (Å)	c_0 (Å)
$CuFeS_2$ (natural)	ours	5.2914 ± 0.0006	10.422 ± 0.004
$CuFeS_2$ (evapolated)	ours	5.21 ± 0.08	10.5 ± 0.3
$CuAlS_2$	ours	5.3335 ± 0.0002	10.4395 ± 0.0008
$CuAlS_2$	16	5.312	10.42
$CuAl_{0.994}Fe_{0.006}S_2$	ours	5.3286 ± 0.0007	10.430 ± 0.003
$CuGaS_2$	ours	5.3519 ± 0.0001	10.4815 ± 0.0004
$CuGaS_2$ (orange)	2	5.328	10.462
$CuGaS_2$ (dark)	2	5.351	10.484
$CuGaS_2$	13	5.351 ± 0.001	10.480 ± 0.005
$CuGa_{0.994}Fe_{0.006}S_2$	ours	5.3499 ± 0.0004	10.479 ± 0.002

Fe (99.99 %) and sulfur. The temperatures of the hot and cold ends were 880°C and 750°C for CuAlS₂ and 870°C and 720°C for CuGaS₂, respectively. After the reaction for two weeks single crystals with the form of column from 1 to 10 mm in length were obtained. The measured lattice constants of Fe-doped CuAlS₂ and CuGaS₂ are given in Table I, together with those of pure CuAlS₂ and CuGaS₂ crystals.

Lattice constants of undoping crystals are in satisfactory agreement with the result of Honeyman,[16] Tell et al.[2] and Schneider et al.[18] which are also shown in Table I. Particularly it is pointed out that lattice constants of CuGaS₂ are in good agreement with those of dark CuGaS₂ which is more close to stoichiometric composition than orange specimens.[2]

§ 3. Experimental Results

Optical absorption measurements of chalcopyrite were made with a single beam infrared spectrometer on an evapolated film.

For the measurements of Fe-doped non-magnetic crystals a Cary 14 recording spectrophotometer was used in the spectral range 0.7 eV~4 eV. A single crystal with a mirror-like face was chosen and from this crystal a long plate-like specimen ranging from 20 to 150 μ in thickness was prepared by the mechanical polishing.

3.1 Absorption spectra of CuFeS₂

The absorption spectrum of chalcopyrite, CuFeS₂, is shown in Fig. 1. There occurs a steep increase of absorption at about 0.6 eV and this is regarded as the absorption edge by Austin et al.[15]

At lower energy region than 0.4 eV an extra absorption can be seen which is due to the sharp absorption of the silica glass substrate at 0.45 eV.

3.2 Absorption spectra of Fe-doped CuAlS₂ and CuGaS₂

In Fig. 1. absorption spectra of three specimens of Fe-doped CuAlS₂ are also given together with that of undoped pure CuAlS₂. At about 3.3 eV the absorption edges are seen for all spectra in satisfactory agreement with the value in the literature.[2,8] For three Fe-doped crystals CuAl₀.₉₃Fe₀.₀₇S₂, CuAl₀.₉₉₄Fe₀.₀₀₆S₂ and CuAl₀.₉₉₉₂Fe₀.₀₀₀₈S₂, a new extra absorption band is observed on the lower energy region of the absorption edge, showing two maxima at 1.3 eV and 2.0 eV. (Hereafter we cite these two strong

absorption peaks as A and B absorptions).

In the case of a heavily doping specimen, CuAl₀.₉₃Fe₀.₀₇S₂, the optical density is so large
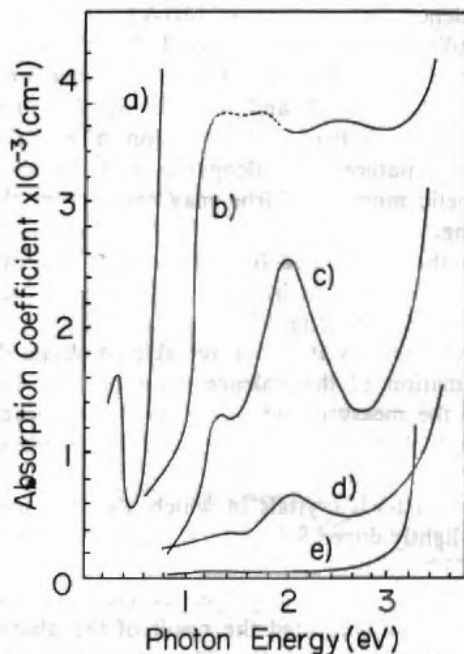
Fig. 1. Absorption spectra of
a) CuFeS₂, b) CuAl₀.₉₃Fe₀.₀₇S₂,
c) CuAl₀.₉₉₄Fe₀.₀₀₆S₂, d) CuAl₀.₉₉₉₂Fe₀.₀₀₀₈S₂ and
e) CuAlS₂.
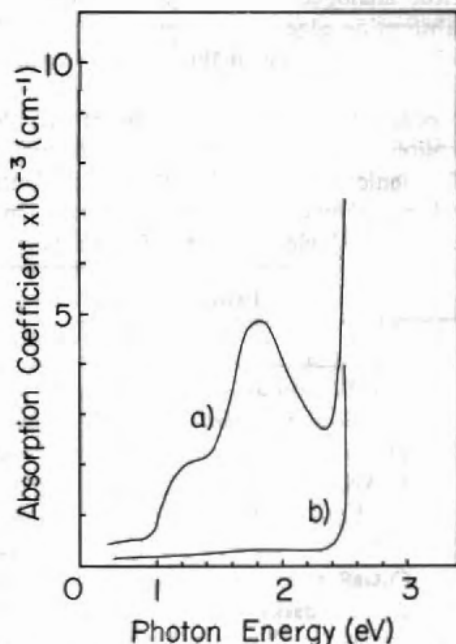
Fig. 2. Absorption spectra of a) CuGa₀.₉₉₄Fe₀.₀₀₆ S₂ and b) CuGaS₂.

that the absorption spectrum becomes very noisy in the spectral range which is shown by the dashed line in Fig. 1.

In Fig. 2, we show the absorption spectra of Ga compounds, $CuGa_{0.994}Fe_{0.006}S_2$ and $GuGaS_2$. Both crystals exhibit a sharp absorption edge at 2.4 eV in good agreement with the results of Tell *et al.*[2] and Bhar.[8] In the Fe-doped $CuGaS_2$ crystal also an additional absorption band occurs at visible region, two maxima locating at 1.2 eV and 1.9 eV.

Schneider reported the black colouration of his ESR specimen, $CuGaS_2$:Fe, caused by a small amount of iron ions. The origin of this colouration is the additional A and B absorptions which we have observed in the visible region.

The intensities of these A and B absorptions are very strong, compared with that encountered in the d-d transitions of magnetic ions. The peak absorption coefficient μ (cm^{-1}) for a transition of oscillator strength f and half-width W (eV) is

$$\mu = \frac{1}{W} \cdot f \cdot N \frac{(n^2+2)^2}{n} \cdot 10^{-17} (cm^{-1}) ,$$

where N is the number of absorption centers per cm^3 and n is the refractive index. When we use 2.45 and 2.67 as the values of the refractive index of $CuAlS_2$ and $CuGaS_2$, respectively,[16,17] the estimated values of oscillator strength are $7.8 \cdot 10^{-2}$ for two Al-compounds and $7.3 \cdot 10^{-2}$ for Ga-compound. As the number of absorbers the nominal concentrations of Fe ions are used for two specimens of Fe-doped $CuAlS_2$, $CuAl_{0.9992}Fe_{0.0008}S_2$ and $CuAl_{0.994}Fe_{0.006}S_2$, and for $CuGa_{0.994}Fe_{0.006}S_2$.

On the basis of nominal concentrations of Fe ions the same oscillator strength is obtained for Al and Ga compounds. This means that the real concentrations of Fe ions do not deviate largely from the nominal ones in these crystals.

3.3 Absorption spectra of Zn- or Mn-doped CuAlS₂ and CuGaS₂ and Fe-doped Ga₂S₃

We made single crystals of $CuAlS_2$ and $CuGaS_2$ which were doped with Mn or Zn ions. Since it is natural to consider Mn and Zn ions to be divalent, the formation of Cu^{2+} ions might be expected from the charge neutrality in these crystals. Then the ionic state is $Cu^+_{1-z}Cu^{2+}_z$ $Al^{3+}_{1-z}Zn^{2+}_zS^{2-}_2$ and so on.

Optical absorption spectra of these crystals are given in Figs. 3 and 4. All of these spectra show no additional peaks corresponding to A and B absorptions of Fe-doped crystals.

A single crystal of iron doped Ga_2S_3 was also made by the chemical transport reaction. This

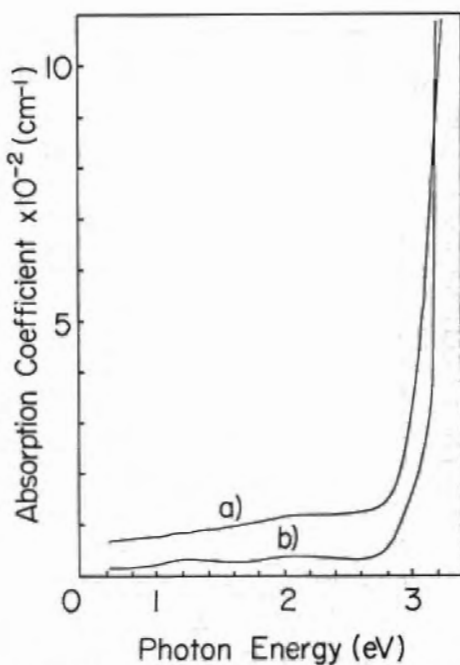Fig. 3. Absorption spectra of a) $CuAl_{0.994}Zn_{0.006}S_2$ and b) $CuAlS_2$.

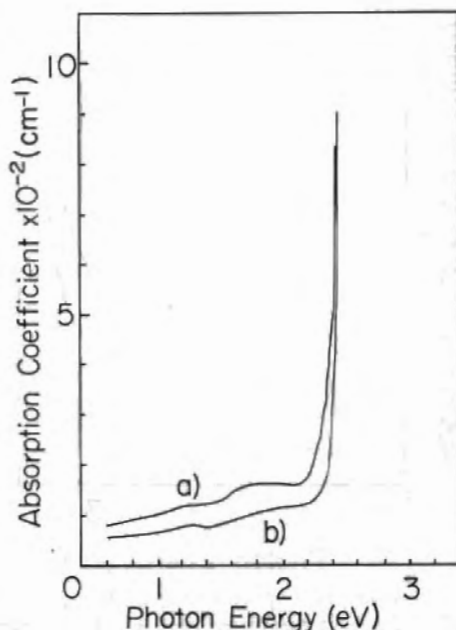Fig. 4. Absorption spectra of a) $CuGa_{0.994}Mn_{0.006}S_2$ and b) $CuGa_{0.994}Zn_{0.006}S_2$.

crystal has not the zincblende type structure but the wurtzite one. However, the latter may be regarded as the only slightly deformed structure from the zincblende and the surroundings around iron ions will not be so different be-
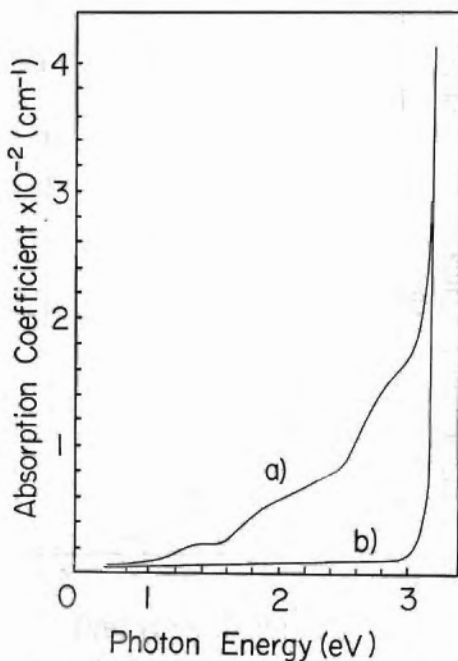

Fig. 5. Absorption spectra of a) Ga_2S_3:Fe and b) Ga_2S_3.
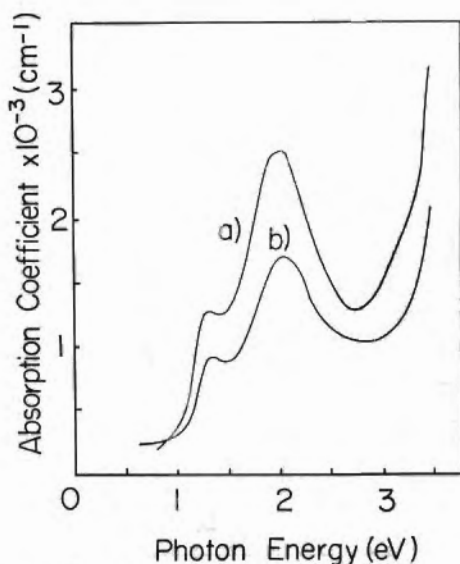

Fig. 6. Absorption spectra of a) $CuAl_{0.994}Fe_{0.006}S_2$ before the heat treatment and b) of the same specimen after the heat treatment in vacuum at 300°C for 2 hours.
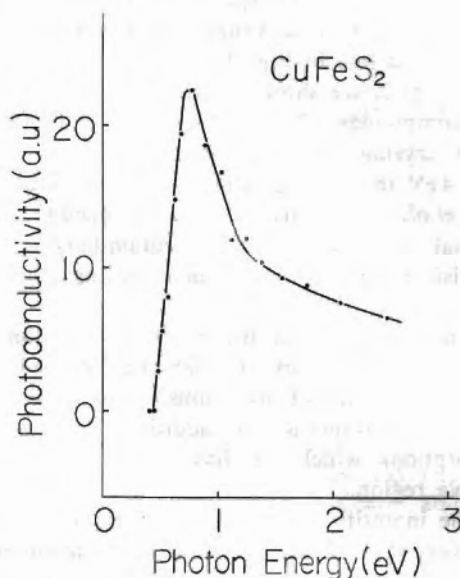

Fig. 7. Photoconductivity spectrum of $CuFeS_2$ at liquid nitrogen temperature.

tween these crystal structures.

The optical absorption of this crystal is observed and the result is shown in Fig. 5, together with that of the undoped Ga_2S_3 single crystal. The additional absorption with three broad maxima at 1.3 eV, 2.0 eV and 2.8 eV appears in the Fe-doped crystal. These absorptions arise clearly from Fe ions and the two lower peaks correspond to A and B absorptions.

3.4 Effect of heat treatment

A single crystal of $CuAl_{0.994}Fe_{0.006}S_2$ was heated at 300°C in vacuum for 2 hours and then quenched. The absorption spectrum of this crystal after the heat treatment is shown in Fig. 6 together with that before the treatment. The intensity of A and B absorptions becomes smaller than that of the specimen before the heat treatment.

3.5 Photoconductivity of $CuFeS_2$

At liquid nitrogen temperature photoconductivity was observed in a natural single crystal of chalcopyrite which had the dark electrical conductivity of 2 $ohm^{-1} cm^{-1}$. The thickness of the specimen was 30 μ and contacts were made with an In amalgam.

The photoconductivity spectrum is shown in Fig. 7. The maximum is located at about 0.7 eV where the absorption edge is also located.

§4. Discussion

In the chalcopyrite and iron doped tetrahedrally

coordinated I-III-VI$_2$ semiconductors there are some contradictory informations for the valence states of magnetic ions. As to the chalcopyrite the mixing state of two extreme ionic states Cu$^+$Fe^{3+}S$_2^{2-}$ and Cu^{2+}Fe^{2+}S$_2^{2-}$ was concluded from the consideration of lattice constants and ionic radii of constituents,[10] while Mössbauer investigations suggested only Fe^{3+} ions.[11,12] Isolated Fe ions lightly doped in the non-magnetic CuGaS$_2$ crystals were evidently in the trivalent state according to ESR experiments.[13]

Since it is difficult to draw a distinct boundary of the valence state of magnetic ions between a lightly doping crystal (CuAl$_{0.93}$Fe$_{0.07}$S$_2$, CuAl$_{0.994}$ Fe$_{0.006}$S$_2$ and so on) and heavily doping or magnetic one (CuFeS$_2$), it should be necessary to take three ions Cu^{2+}, Fe^{2+} and Fe^{3+} into consideration as the absorbing centre of these compounds. Now the effect on the optical absorption of these ions is examined on the bases of present observations.

The evaporated film of CuFeS$_2$ shows the absorption edge at 0.6 eV which is in good agreement with that reported by previous authors.[14,15]

The most salient feature which we observe in the Fe-doped I-III-VI$_2$ semiconductors is the extra absorption band (A and B absorptions) at the low energy region of the absorption edge (See Figs. 1 and 2). Its oscillator strength estimated at $7 \cdot 10^{-3}$ is so large that this absorption does not result from typical d-d transitions of isolated magnetic ions but from the charge transfer transitions relating to 3d electrons.

The intensity of A and B absorptions increases with the increase of doped Fe ions and grows into the absorption edge of CuFeS$_2$. The existence of photoconductivity (Fig. 7) would suggest that in chalcopyrite the absorption edge is due to the band-to-band transition including 3d electrons. Though the type of this photo-conduction is not yet clear, it is considered that the conduction band would be composed of 3d orbitals if the photoconduction is of N-type.

Broser have found a broad absorption band just at the same energy region in Cu-doped ZnS and assigned this absorption to be the charge transfer transition from Cu^{2+} ions.[16] However, by using the facts that Mn- or Zn-doped CuAlS$_2$ and CuGaS$_2$ have no extra absorption in these energy region (see Figs. 3 and 4) and a Fe-doped Ga$_2$S$_3$ crystal has extra absorptions corresponding to A and B absorptions (see Fig. 5) it is concluded that A and B absorptions do not relate to Cu ions, but to Fe ions. This situation is probably the same in CuFeS$_2$.

The origin of the decrease in absorption intensity of a Fe-doped CuAlS$_2$ crystal after the heat treatment is interpreted as follows (see Fig. 6): By the heat treatment in the reducing atmosphere some amounts of Fe^{3+} ions in the crystal are reduced into Fe^{2+} ions. In the energy region from 0.6 eV to 2.8 eV there occurs no absorption of Fe^{2+} ions according to the observation in the Fe-doped ZnS.[19] Consequently the increase of Fe^{2+} ions reduces the intensities of A and B absorptions at 1.3 eV and 2.0 eV. In other words this fact will be the evidence that A and B absorptions do not result from Fe^{2+} ions but from Fe^{3+} ions.

When a coactivator (for example, iodine) is added in an Fe-doped ZnS crystal it shows three broad absorption peaks at about 2.9 eV, 2.0 eV and 1.5 eV, the last two of which locate just at the same energy region of A and B absorptions of Fe-doped CuAlS$_2$ and CuGaS$_2$.[20] Though it is not clearly understood whether Fe^{2+} ions turn into trivalent states by the introduction of iodine ions these absorptions might be resulted from Fe^{3+} ions, because the luminescence of this specimen was attributed to Fe^{3+} ions.[20]

In conclusion it is pointed out that strong A and B absorptions of Fe-doped CuAlS$_2$ and CuGaS$_2$ are due to the charge transfer transitions from Fe^{3+} ions and the absorption edge of CuFeS$_2$ is the foot of band to band transition corresponding to this charge transfer transition. Since the conduction band made from 3d orbitals is not as wide as that of ordinary semiconductors, small value of Hall mobility of CuFeS$_2$ may result. The fact that the magnetic susceptibility is nearly temperature independent and does not obey the Curie-Weiss law[9,21] is also possibly the result of this narrow d-band. Nevertheless, these electrical and magnetic properties of chalcopyrite are very interesting to be investigated in detail in future.

Acknowledgement

crystals and continuous encouragement and to Dr. T. Sakurai for use of his computer programme to calculate lattice constants.

References

1) C. H. L. Goodman: J. Phys. Chem. Solids 6 (1958) 305.

2) B. Tell and J. L. Shay: Phys. Rev. B4 (1971) 2463.

3) J. L. Shay, B. Tell, H. M. Kasper and L. M. Shiavone: Phys. Rev. B5 (1972) 5003.

4) J. L. Shay and H. M. Kasper: Phys. Rev. Letters 29 (1972) 1162.

5) G. C. Bhar and R. C. Smith: Phys. Status solidi (a) 13 (1972) 157.

6) cf. the controversial discussions concerning the existence of AgFeTe$_2$: V. P. Zhuze, V. M. Sergeeva and E. L. Shtrum: Soviet Physics -Techn. Phys. 3 (1958) 208; S. H. Wernick and R. Wolfe: J. appl. Phys. 32 (1961) 749; E. L. Shtrum: Soviet Physics -Solid State 2 (1961) 1352; P. Manca and F. Massazza: J. appl. Phys. 33 (1962) 1608; A. Rabenau and K. Deneke: Angew. Chem. 74 (1962) 659; E. L. Shtrum: J. appl. Phys. 35 (1964) 252; P. Manca and F. Massazza: J. appl. Phys. 36 (1965) 647; K. Deneke: J. appl. Phys. 36 (1965) 653. CuFeSe$_2$ is known as a mineral eskebornite. The systematic absences of X-ray diffraction lines of eskebornite are different from those of chalcopyrite.

7) B. I. Boltaks and N. N. Tarnovskii: Zhur. tekhn. Fiz. 25 (1955) 402.

8) T. Teranishi: J. Phys. Soc. Japan 16 (1961) 1881.

9) G. Donnay, L. M. Corliss, J. D. H. Donnay, N. Elliott and J. M. Hastings: Phys. Rev. 112 (1958) 1917.

10) L. Pauling and L. O. Brockway: Z. Krist. 82 (1932) 188.

11) E. Frank: Nuovo Cimento 63 B (1968) 407.

12) D. Raj, K. Chandra and S. P. Puri: J. Phys. Soc. Japan 24 (1968) 39.

13) J. Schneider, A. Räuber and G. Brandt: J. Phys. Chem. Solids 34 (1973) 443.

14) C. H. L. Goodman and R. W. Douglas: Physica 20 (1954) 1107.

15) I. G. Austin, C. H. L. Goodman and A. E. Pengelly: J. electrochem. Soc. 103 (1956) 609.

16) W. N. Honeyman: J. Phys. Chem. Solids 30 (1969) 1935.

17) W. N. Honeyman and K. H. Wilkinson: J. Phys. D 4 (1971) 1182.

18) I. Broser, K. H. Franke and H. J. Schulz: II-VI Semiconducting Compounds (Benjamin, New York, 1967) p. 81.

19) G. A. Slack, F. S. Ham and R. M. Chrenko: Phys. Rev. 152 (1964) 376.

20) P. M. Jaffe and E. Banks: J. electrochem. Soc. 111 (1964) 52.

21) R. Adams, P. Russo, R. Arnott and A. Wold: Mat. Res. Bull. 7 (1972) 93.