Polarized Absorption Spectra of CuGaS$_2$: Co^{2+}

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Optical absorption spectra are observed for Co^{2+} ion in CuGaS$_2$ and their brief analysis is given in the framework of the ligand field theory. The polarization dependence of the spectra is elucidated in the vicinity of the [$^4T_1$(1)] band ($\sim$7,000 cm^{-1}) and of the [$^4T_1$(2), $^2T_2$(1), $^2A_1$] band ($\sim$13,000 cm^{-1}) at 2 K. The adjusted values of low symmetry (D_{2d}) crystal field parameters are $\langle\zeta|V(D_{2d})|\zeta\rangle = 132$ cm^{-1} and $\langle v|V(D_{2d})|v\rangle = -100$ cm^{-1}.

§1. Introduction

We have been studying the optical properties of an antiferromagnetic semiconductor CuFeS$_2$ and non-magnetic I-III-VI$_2$ compounds doped with transition metal impurities, in order to know the electronic structures and to get insight into magnetic and semiconductive behaviors of CuFeS$_2$.[1-8] In the previous paper[9] (hereafter referred to as I), we reported the experiments of unpolarized light absorption on CuGaS$_2$: Co^{2+} and the results of their theoretical analysis. The two main bands observed were assigned to the transitions to the $^4T_1$(1) and $^4T_1$(2) levels, respectively: The complicated structure of the latter was attributed to the fact that the $^4T_1$(2) level was mixed with closely lying levels, $^2T_2$(1) and $^2A_1$, to constitute a level bunch. Although some ambiguity was unavoidable in our assignment of observed fine structures of such unpolarized spectra, we obtained tentatively estimates of the low symmetry parameters. The values of these parameters were smaller by an order than the cubic field parameter as expected in ref. 7.

In the present article we report polarized light absorption spectra of the same substance CuGaS$_2$: Co^{2+} at 2 K in the energy region up to the fundamental absorption edge ($\sim$20,000 cm^{-1}), and analyse the $^4T_1$(1) band ($\sim$7,000 cm^{-1}) and the $^4T_1$(2) level bunch band ($\sim$13,000 cm^{-1}) in the framework of the ligand field theory. The analysis yields low symmetry crystal field parameters, $\langle\zeta|V(D_{2d})|\zeta\rangle =$ 132 cm^{-1} and $\langle v|V(D_{2d})|v\rangle = -100$ cm^{-1}, which reproduce the fine structure of the observed spectra.

§2. Experiments

Single crystals of CuGaS$_2$: Co^{2+} were grown by the chemical transport method as stated in I. Although the nominal concentration of Co ion was 0.4 mole%, the actual concentration seems to vary from sample to sample, resulting in wide variety of absorption intensities.

Most of the crystals were obtained in the form of thin facets. The natural surface was determined as {112} by means of the X-ray Laue photography. Optical absorption spectra were obtained from the {112} face of the crystal for the polarized light $E//c'$ and $E\perp c$, where c' denotes the projection of c-axis on the {112} face; the former makes an angle of 35.8° with the latter. The location of the c'-axis was determined by use of the polarization dependence of the fundamental absorption edge of CuGaS$_2$ reported by Shay et al.,[10] in addition to the X-ray Laue methods.

Samples were polished to 50 μm thickness, and were immersed in the liquid helium dewar. The absorption measurements were performed by means of the conventional single beam photoelectric system; a halogen tungsten lamp, a Nikon-P250 monochromator, a photomultiplier (Hamamatsu R636 GaAs type) for the upper absorption band, a liquid nitrogen-cooled InSb photovoltaic cell (Judson J-10D) for the lower band, a phase sensitive detector (PAR

124) and a Gran prism polarizer (Halle Inc.).

Absorption spectra between 13,000 cm^{-1} and 20,000 cm^{-1} measured at 2 K are shown in Fig. 1. Solid curves and broken curves represent $E//c'$ and $E \perp c$ spectra respectively. Steep rise of absorption around 19,500 cm^{-1} with distinctive polarization dependence corresponds to the fundamental absorption edge of the host crystal. In the low energy side of the absorption edge there lies an intense structureless band ranging from 15,000 cm^{-1} to 18,000 cm^{-1}. In the lower energy side of the band there exists the level bunch band with considerable fine structure as reported in I. Roughly speaking, there are absorption peaks around 13,300 cm^{-1}, 13,600 cm^{-1}, 13,900 cm^{-1} and 14,300 cm^{-1}, of which the first one shows the most conspicuous polarization dependence. Magnified spectra in the vicinity of the first peak are given in Fig. 2.

The lower absorption band around 7,000 cm^{-1} consists of three absorption lines located at 6,600 cm^{-1}, 6,900 cm^{-1} and 7,600 cm^{-1}, as shown in Fig. 3. Polarization dependence of this band was not so distinctive as that of the higher energy band.

§3. Theoretical Analysis

3.1 The calculation of the energy levels

Theoretical treatments are essentially the same as those worked in I. Taking account of the spin-orbit interaction and the low symmetry
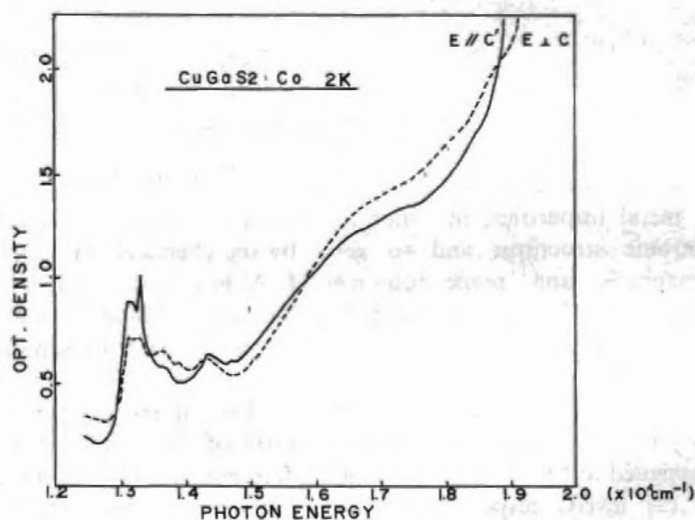

Fig. 1. Polarized absorption spectra of CuGaS$_2$: Co^{2+} at 2 K in the energy region between 12,000 cm^{-1} and 20,000 cm^{-1} as obtained from a {112} face. Solid curve—$E//c'$; broken curve—$E \perp c$.
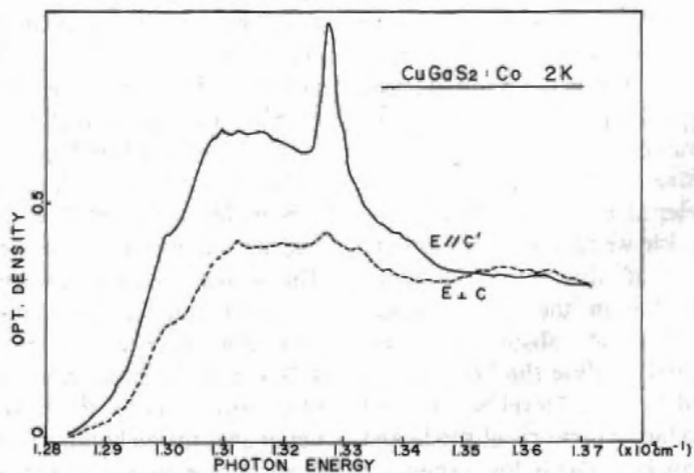

Fig. 2. Details of the $^4A_2 \rightarrow [^4T_1(2), ^2T_2(1), ^2A_1]$ absorptions. Solid curve—$E//c'$; broken curve—$E \perp c$.
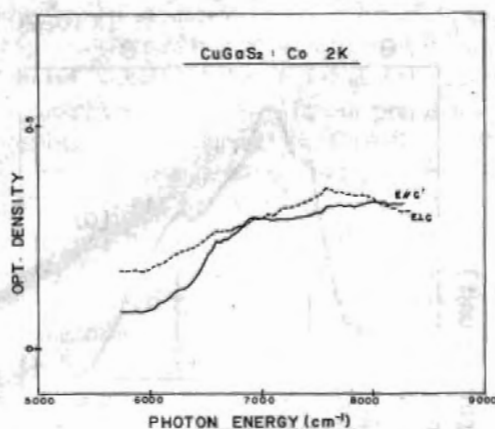
Fig. 3. $^4A_2$—$^4T_1$(1) absorptions of Co^{2+} in CuGaS$_2$ at 2 K. Solid curve—$E//c'$; broken curve—$E \perp c$.

(D_{2d}) crystal field as well as the Td field, we calculate the energy levels of a Co^{2+} in the framework of the conventional ligand-field theory. The parameters of the interatomic Coulomb repulsion, the crystal field strength, etc. are determined so that they reproduce, as exactly as possible, the fine structure of the observed spectra including, particularly, the detailed features of the dependence on the polarization of light.

In the following we summarize the values of the parameters adopted in these calculations. They are listed in Table I, together with those used for ZnS: Co^{2+} by Weakliem.[11]

First of all, $B=500$ cm^{-1} and $Dq=430$ cm^{-1}, which are the same as taken in I, are determined from, mainly, the peak positions of two absorption bands.

The newly adopted value $C=2,500$ cm^{-1} ($C/B=5.0$) turns out to be more suitable to get the observed width of the upper band. Previously in I, we used $C/B=4.4$ which was obtained for ZnS: Co, since our observed data were rather obscure at that time, as far as the

Table I.   List of the parameters adopted for CuGaS$_2$: Co^{2+} in the present study and for ZnS: Co^{2+} by Weakliem.[11]

Parameters	CuGaS$_2$: Co^{2+}	ZnS: Co^{2+}
Dq (cm^{-1})	430	375
B (cm^{-1})	500	610
C/B	5	4.4
ζ (cm^{-1})	595.5	585
P (cm^{-1})	229	—
Q (cm^{-1})	−200	—

width of the upper band was concerned.

We use for the spin-orbit interaction parameter $\zeta=595.5$ cm^{-1} which we determined in I from the zero-field splitting constant D and the g-factor obtained by Kaufmann et al.[12] This value is larger than the free ion value $\zeta_0=533$ cm^{-1}. It has been turned out, however, that a larger value is preferable to explain the width of the observed absorption bands, especially of the lower band.

Low symmetry field parameters used are as follows:

$$Q=2\langle v|V(D_{2d})|v\rangle=-200 \text{ cm}^{-1}$$

$$P=\sqrt{3}\langle\zeta|V(D_{2d})|\zeta\rangle=229 \text{ cm}^{-1}.$$

The calculated intensity patterns of the upper and lower bands are well reproduced for any value of Q within the region, say $-300\leq Q\leq -100$. We choose somewhat arbitrarily the center value of the region. As for P, the calculated patterns hardly depend on the parameter in very wide regions. Therefore it seems reasonable to determine P by the relation

$$X_0\equiv\left(\frac{1}{\sqrt{3}}\right)P-\left(\frac{1}{2}\right)Q=232.2 \text{ cm}^{-1}$$

which was obtained in I from consideration of g-values, $g_{//}$ and $g_{\perp}$.

3.2   The calculation of the intensity patterns

Since the zero-field splitting parameter D is positive according to I, the lowest levels of the ground state are $|^4A_2, m_s=\pm\frac{1}{2}\rangle$ which have the Γ_7 symmetry of D_{2d} double group representation. The matrix element of the transition dipole remains considerable only for the transition $^4A_2\rightarrow{}^4T_1(2)$, and it vanishes for the transition to other members, $^2T_2(1)$ and $^2A_1$, in the level bunch responsible for the higher energy band.

The intensity patterns calculated on the assumption that only the lowest doublet $|^4A_2, m_s=\pm\frac{1}{2}\rangle$ of the ground state are occupied are illustrated by the vertical lines in Figs. 4 and 5, where for comparison the solid curves are shown to indicate the experimental patterns corrected by subtracting the superimposed background.

§4.   Discussions
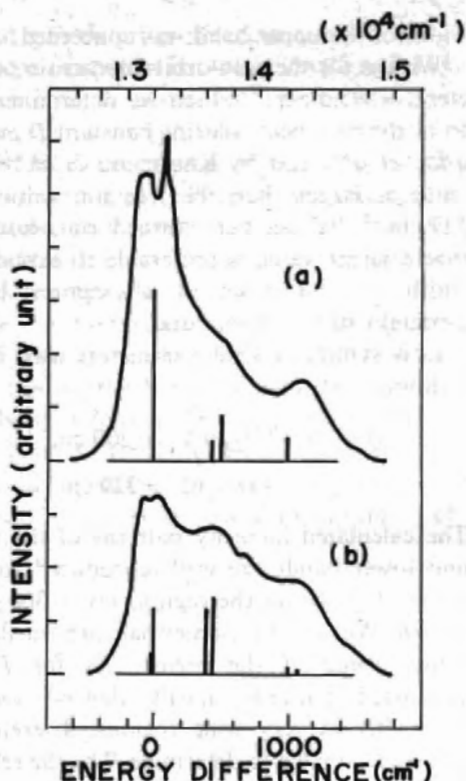
The calculated spectra agree with the ob-

Fig. 4. Comparison of the $[^4T_1(2), {}^2T_2(1), {}^2A_1]$ spectra with the theoretical predictions. (a) $E//c$ spectrum, (b) $E \perp c$ spectrum. Corrections have been made to subtract the overlapping foot of the broad band at higher energies.

Fig. 5. Comparison of the $^4T_1(1)$ spectra with the theoretical predictions. (a) $E//c$ spectrum, (b) $E \perp c$ spectrum. Back-ground corrections have been made.

served ones satisfactorily as far as the essential features of the two $^4T_1$ bands are concerned, as seen in Figs. 4 and 5. The $^4T_1(2)$ level bunch band, however, seems to consist of more absorption lines than those expected from the calculation as seen in Fig. 2. These extra lines arise possibly from superposition of the absorption lines for the different Co^{2+} centers accessible in a $CuGaS_2$ crystal containing some imperfections such as stacking faults and vacancies: Kazanskii *et al.*[13] interpreted the absorption spectra of $ZnS: Co^{2+}$ as superposition of the contributions due to the different Co^{2+} centers in the crystal containing stacking faults; besides the charge neutrality rule in $CuGaS_2$, in contrast to ZnS, requires some vacancies, whichever cations Co^{2+} ions substitute, Cu^+ or Ga^{3+}. In fact, the low energy side structures of the $^4T_1(2)$ band are slightly sample-dependent. This might favor to ascribing these structures to certain imperfections.

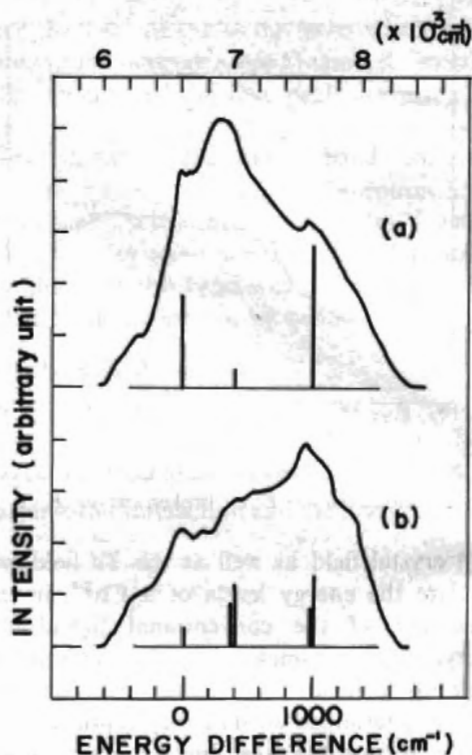It is necessary to explain the width of the

absorption bands that the spin-orbit parameter ζ assumes a slightly larger value than the free ion value, $\zeta_0 = 533$ cm^{-1}. Koidl *et al.*[14] have shown that the account of a weak Jahn-Teller coupling can explain the observed spectra of $ZnS: Co^{2+}$ with the less values of ζ than ζ_0. They have also shown that there appear in absorption spectra several vibronic transition lines which are not expected for the static crystal field model. Although their theory is not directly applicable to our case where surroundings of a Co^{2+} ion are statically distorted even in its non-degenerate ground state, the dynamical Jahn-Teller coupling could play some important role to understand the fine structure completely since the low symmetry crystal field is rather weak and comparable to the Jahn-Teller coupling strength they assumed for the ZnS crystal.

The intense structureless absorption band at photon energy region between 15,000 cm^{-1} and 18,000 cm^{-1} cannot be assigned successfully to any crystal field levels; although the levels $^2T_1(2)$, $^2T_2(2)$, $^2E(2)$ and $^2T_1(3)$ lie in this

energy region as shown in Fig. 4 of ref. 9, the intensity corresponding to spin-forbidden transitions to these levels must be much weaker than the observed intensity. In our preliminary absorption measurements on CuAlS$_2$: Co^{2+}, the structureless band (15,000 cm^{-1} ~ 18,000 cm^{-1}) has not been observed, although the two $^4T_1$ bands lie very close to those of CuGaS$_2$: Co^{2+}, but the absorption edge has been seen shifted by an amount of 5,000 cm^{-1} from the original edge of CuAlS$_2$ (~25,000 cm^{-1}). Neither such band nor such edge shift has been reported for ZnS: Co^{2+}.

Cobaltous ions substituting Ga^{3+} and Cu$^+$ may be accompanied with some ion vacancies to satisfy the charge neutrality, as pointed out in the first paragraph of this section, whereas naked Co^{2+} ions, not accompanied with vacancies, can become donors or acceptors. Trapped electrons into anion vacancies, deep donor states, or acceptors are known to give rise to a broad absorption band in the low energy side of the absorption edge. It is quite probable that the band under consideration is related to one or another of these possibilities. It should be remarked that the ionization of donor or acceptor states can be regarded, in the cluster model, as a charge transfer transition which is of the same type as we treated in the consideration of CuGaS$_2$: Fe.[8] Detailed interpretations will be discussed in later publications.

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