Reflectance Magneto-Circular Dichroism of $CdCr_2Se_4$

Katsuaki SATO

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

(Received May 18, 1977)

Reflectance magneto-circular dichroism (R-MCD) spectrum of $CdCr_2Se_4$ has been studied in the energy region between 0.9 and 4.1eV. The off-diagonal element of the dielectric tensor calculated from the R-MCD data showed a number of structures over the energy range. At the absorption edge region were observed a few fine structures suggesting that localized states were involved in the corresponding transition.

A number of optical, photoconductive and magneto-optical studies have been reported on the ferromagnetic semiconductor $CdCr_2Se_4$.[1-6] There has been, however, a long controversy whether the red-shifting absorption edge is related to the band-to-band transition or to the localized one such as the charge transfer transition.

The author has recently measured the reflectance magneto-circular dichroism spectrum (hereafter it is referred to as R-MCD) of $CdCr_2Se_4$ in order to get information on the electronic structures of the material.

The R-MCD measurements were carried out by means of the polarization-modulation technique employing a CaF_2-piezobirefringent modulator.[7] The measured sample was a single crystal of $CdCr_2Se_4$ obtained by the chemical vapor transport method described by Wehmeier *et al.*[8] Magnetization of the sample was saturated in a superconducting solenoid with a field of 10 kOe at liquid helium temperature. The angle of incidence at reflection was 5°, which provided a nearly-normal incidence condition. The reflected beam was detected by a photomultiplier ($\lambda<920$ nm) or a cooled InSb photovaltaic cell ($\lambda>700$ nm). The data were stored on the perforated tape and were processed by an IBM370 computor.

The results are shown in Fig. 1. The solid curve represents the R-MCD, $\Delta R/R$; here $\Delta R=R^+-R^-$, and $R=(R^++R^-)/2$, where R^+ and R^- denote the reflectivity for the right-circularly polarized light (RCP) and the left-circularly polarized light (LCP), respectively. The dotted curve illustrates $\Delta\theta=\theta^+-\theta^-$, where θ^+ and θ^- represent the phase shift

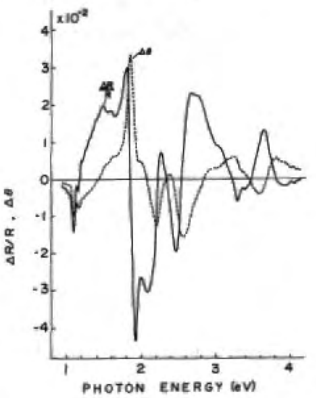

Fig. 1. The R-MCD spectrum (solid curve) and the calculated phase shift difference spectrum (dotted curve) of $CdCr_2Se_4$ at liquid helium temperature.

for RCP and LCP, respectively, calculated from the $\Delta R/R$-spectrum by using the dispersion relation derived by D. Y. Smith.[9]

Note that there hold simple relations between the MCD parameters and Kerr parameters as follow:

$$\left.\begin{aligned}\Delta\theta&=-2\phi\\ \frac{\Delta R}{R}&=4\eta\end{aligned}\right\}, \tag{1}$$

where ϕ and η denote Kerr-rotation and Kerr-ellipticity, respectively.

Phenomenologically the magneto-optical effect of an isotropic medium is described by a dielectric tensor,[10]

$$\varepsilon=\begin{pmatrix}\varepsilon_0 & -i\varepsilon_1 & 0\\ i\varepsilon_1 & \varepsilon_0 & 0\\ 0 & 0 & \varepsilon_z\end{pmatrix}, \tag{2}$$

where $\varepsilon_0=\varepsilon_0'+i\varepsilon_0''$ and $\varepsilon_1=\varepsilon_1'+i\varepsilon_1''$. The real and imaginary parts of the off-diagonal

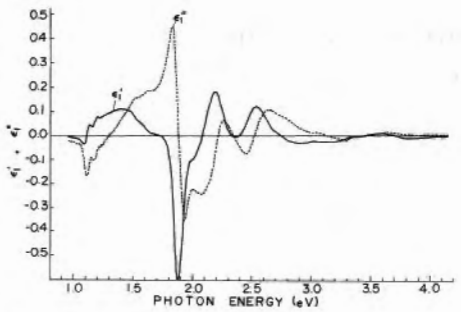

Fig. 2. The calculated spectral dependence of real (ε_1') and imaginary (ε_1'') parts of the off-diagonal element of the dielectric tensor of $CdCr_2Se_4$.

element ε_1, which give rise to the magneto-optical effect, can be expressed as linear combinations of $\Delta R/R$ and $\Delta\theta$ by equations,[11]

$$\left.\begin{aligned}\varepsilon_1' &= -\frac{1}{4}\left\{n(1-n^2+3k^2)\frac{\Delta R}{R} - 2k(1-3n^2+k^2)\Delta\theta\right\}\\ \varepsilon_1'' &= -\frac{1}{4}\left\{k(1-3n^2+k^2)\frac{\Delta R}{R} + 2n(1-n^2+3k^2)\Delta\theta\right\}\end{aligned}\right\}. \quad (3)$$

In Fig. 2 are given spectral dependences of ε_1' and ε_1'' as calculated from equations (3), using the values of n and k obtained by Itoh *et al.* from their straight reflectivity data.[5] For historical reasons magneto-optical line shapes are classified as paramagnetic or diamagnetic; they are referred to as paramagnetic if ε_1' is dispersive and ε_1'' is dissipative, whereas those with dissipative ε_1' and dispersive ε_1'' are as diamagnetic.[10]

In Fig. 2 diamagnetic terms can be seen at 1.3, 1.88, 2.19, 2.53, 2.90 and 3.13 eV. There exist a number of additional structures in the higher energy region.

The structure at 1.3 eV, which corresponds to the absorption edge of the crystal has a few fine structures with paramagnetic line shape superposed on its low energy side; 1.105 and 1.165 eV. Sharpness of these fine structures implies that corresponding transitions are localized ones rather than band-to-band transitions. The broad band around 1.3 eV can be considered to consist of a bunch of such localized transitions, of which only the edge portion is resolved. This situation is similar to the case of Europium chalcogenides in which the magneto-optical structures of absorption edge have been explained in terms of a bunch of localized transitions associated with the magnetic exciton.[12] Structures at 1.18, 2.19 and 2.53 eV, on the other hand, may be assigned to band-to-band transitions, since at these photon energies intense absorption has been reported to exist[5] and the energy position of the most prominent diamagnetic structure (1.88 eV) is very close to the band gap (1.83 eV) of CdSe which has similar surroundings of Cd site as those of $CdCr_2Se_4$; both having a tetrahedral symmetry with nearly the same Cd–Se distance. Assignments stated above do not agree with those by Stoyanov *et al.* who attributed both structures at the absorption edge and at 2 eV found in their thermoreflectance spectrum to band-to-band transitions.[6]

Further analysis of the R-MCD data requires more quantitative knowledge of the electronic structure of the magnetic semiconductor, than those in previous studies. The molecular-orbital calculation in the atomic cluster has recently been proved to be a powerful tool for understanding the optical properties of a magnetic semiconductor $CuFeS_2$.[13] The same kind of calculation on $CdCr_2Se_4$ should possibly help further assignments and is now in progress by T. Kambara and his colleagues. Detailed discussion of the present data will be reported in later publications.

References

1) G. Harbeke and H. W. Lehmann: Solid State Commun. **8** (1970) 1281.
2) K. Sato and T. Teranishi: J. Phys. Soc. Japan **29** (1970) 523.
3) S. Wittekoek and P. F. Bongers: IBM J. Res. Develop. **14** (1970) 312.
4) K. Ahrenkiel, F. Moser, S. Lyu and C. R. Pidgeon: J. appl. Phys. **42** (1971) 1452.
5) T. Itoh, N. Miyata and S. Narita: Japan. J. appl. Phys. **12** (1973) 1265.
6) S. G. Stoyanov, M. N. Iliev and S. P. Stoyanova: Phys. Stat. Solidi (a) **30** (1975) 133.
7) S. N. Jasperson and S. E. Schnatterly: Rev. Sci. Instr. **40** (1969) 761.
8) F. H. Wehmeier: J. Crystal Growth **5** (1969) 26.
9) D. Y. Smith: J. Opt. Soc. America **66** (1976) 547.
10) G. B. Scott, D. E. Lacklison, H. L. Ralph and J. L. Page: Phys. Rev. B **12** (1975) 2562.
11) Similar formulas have been derived by S. Wittekoek *et al.* in Phys. Rev. **12** (1975) 2777. Note that their definition of the off-diagonal tensor element differs in sign from equation (2).
12) T. Mitani, M. Ishibashi and T. Koda: J. Phys. Soc. Japan **38** (1975) 731.
13) T. Kambara: J. Phys. Soc. Japan **36** (1974) 1625.