High Field Magnetooptics of Diluted Magnetic Semiconductors(Magnetooptics)

High Field Magnetooptics of Diluted Magnetic Semiconductors*

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Synopsis

Absorption and luminescence spectra of $Cd_{1-x}Mn_xSe$ (x=0.10 and 0.38) and reflectance spectra of $Cd_{1-x}Co_xSe$ (x=0.012) were investigated in high magnetic fields up to 25 T by a hybrid magnet and a magnetospectrometer with an optical fiber system.

I. Introduction

A diluted magnetic semiconductor (DMS) is a II-VI or IV-VI compound in which the group II or IV cations are replaced in part by magnetic ions such as manganese. Ever since the first report on $Hg_{1-x}Mn_xTe$,[1] the DMS systems have excited scientists because of their novel properties;[2] a giant effective g-value, a large Zeeman splitting of energy bands and formation of magnetic polaron. These properties come from the exchange interaction between a band electron and a localized magnetic ion (sp-d exchange interaction).

The magnetooptical properties of the wide gap DMSs, such as $Cd_{1-x}Mn_xTe$ (zinc blende structure) and $Cd_{1-x}Mn_xSe$ (wurzite structure), have been studied over wide spectral range from the infrared to ultraviolet to investigate the sp-d exchange interaction. Aggarwal et al.[3] measured the reflectance spectra of $Cd_{1-x}Mn_xSe$ in magnetic fields up to 15 T and estimated the sp-d exchange constant. Heiman et al.[4] studied the behavior of the bound and free exciton in the magnetoluminescence spectra of $Cd_{1-x}Mn_xSe$.

In this paper we report the absorption and luminescence spectra of $Cd_{1-x}Mn_xSe$(x=0.10 and 0.38) and the reflectance spectra of $Cd_{1-x}Co_xSe$ (x=0.012) in magnetic fields up to 25 T. The high field magnetooptical measurements are expected to reveal the excitonic behavior of the optical transition in a magnetic field; a linear Zeeman splitting and a diamagnetic shift, which are undistinguishable in the low field region because of the large sp-d interaction. Research on $Cd_{1-x}Co_xSe$ has been stimulated by the question whether the magnetic and optical properties observed in $Cd_{1-x}Mn_xSe$ are intrinsic in the DMS or not.

II. Experimental

Single crystals were grown by the Bridgman technique. The x-values of $Cd_{1-x}Mn_xSe$ were determined by microprobe and x-ray fluorescence. The x-value of $Cd_{1-x}Co_xSe$ was

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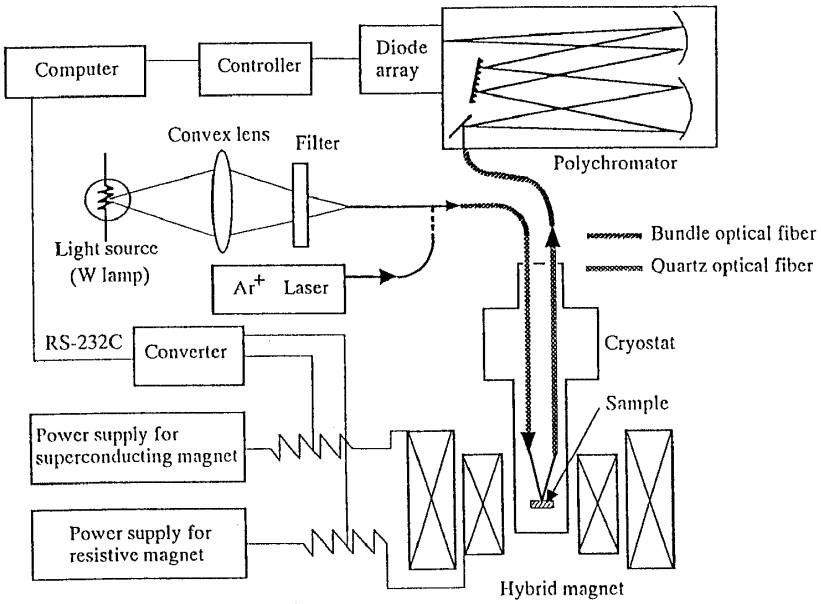

Fig.1. Magnetooptical spectrometer with the hybrid magnet.

determined by the saturation magnetization. The sample faces were polished mechanically and then etched in a methanol solution containing 1% bromine.

Magnetic fields were produced by a hybrid magnet in the High Field Laboratory. Figure 1 shows the magnetooptical system which consists of light sources, flexible bundles of optical fibers to bring the light into and out of the cryostat within the magnet, a grating spectrometer (Jobin-Yvon THR-1000S) and a PCD linear image sensor (Hamamatsu S2304-1024Q). These were common in absorption, fluorescence and reflectance measurements. A tungsten-halogen lamp or a xenon lamp was used with an interferometric band-pass filter as a light source for the absorption and reflectance measurements. An argon ion laser was used for the luminescence measurement.

The optical systems in the cryostat for the luminescence and reflectance measurements are shown in Fig.2(a) and (b), respectively,

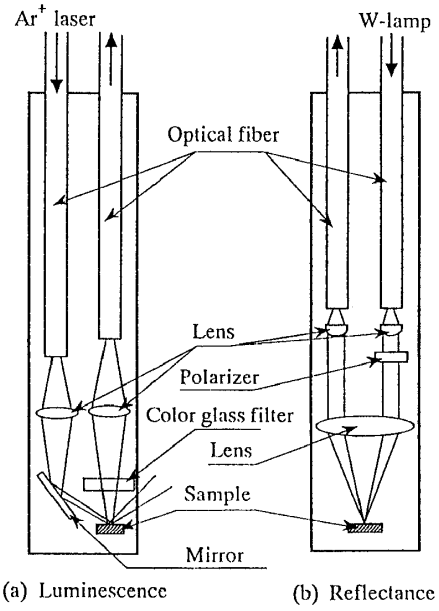

Fig.2. Optical systems in the cryostat for (a) magnetoluminescence and (b) magneto-reflectance measurements.

where both systems are the Faraday configuration. Quartz optical fibers of 1 mm core were employed as a light guide. The light out of the fiber was focused on the sample and the emitted or reflected light was collected into the other fiber by convex lenses. Details of the absorption measurements were described elsewhere.[5)]

Magnetizations were measured at 4.2 K by a sample-extraction method with the hybrid magnet. The same sample for each x value was used for both optical and magnetization measurements to eliminate experimental errors resulting from slight difference of the x value from sample to sample.

III. Theoretical Background

Since $Cd_{1-x}Mn_xSe$ is a direct-gap semiconductor with the wurzite structure, the relevant band structure for the optical transition occurs at the Γ point of the Brillouin zone, as shown in Fig.3. The valence band is split by the crystal field into subbands referred to as A and B, which give rise to A and B excitons. The valence and conduction bands are further split by the magnetic field H. In this paper we consider the optical transition only for H//c. In that case the selection rule of the polarization for each transition is also given in Fig.3, where the π polarization represents e//c (**e** is the electric vector of the light), and the labels σ^+ and σ^- denote circular polarizations corresponding to Δm_j=+1 and Δm_j=-1, respectively.

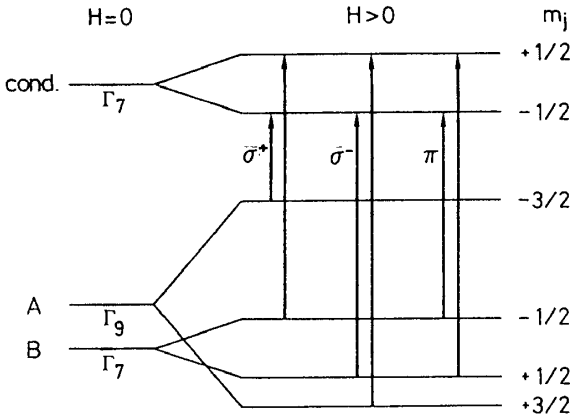

Fig.3. Schematic of the energy levels at Γ for the wurzite structure.

The conduction and valence band splittings due to the sp-d interaction have been analyzed by Aggarwal et al. for the case of the wurzite DMS.[3)] We have followed their analysis to compute the energy levels of the conduction and valence bands. In the case of H//c the energy matrices of both bands are simply diagonalized and their energies are written as follows;

$$\begin{aligned} E_{\mathrm{cond}} &= E_g \pm G_e, \\ E_A &= \pm G_h, \\ E_B &= -\frac{\Delta_1 + 3\Delta_3}{2} + E_{\pm}, \end{aligned} \qquad (1)$$

where

$$G_e = \frac{1}{2} N_0 \alpha x < S_z >,$$
$$G_h = \frac{1}{2} N_0 \beta x < S_z >, \qquad (2)$$
$$E_\pm = \left[\left[\frac{(\Delta_1 - \Delta_2) \pm 2G_h}{2} \right]^2 + 2\Delta_3^2 \right]^{1/2}$$

In eq.(1) E_g denotes the band gap energy in the absence of magnetic field. In eq.(2) N_0 is the density of cation; α and β are the sp-d exchange integrals for the conduction and valence bands, respectively; $<S_z>$ is the magnitude of the thermal average of spins of magnetic ions; Δ_1 is the crystal-field splitting constant; Δ_2 and Δ_3 are constants of the spin-orbit interaction.

The A exciton energy for the σ^+ and σ^- polarizations can be described as;[6]

$$E_{A\sigma^\pm} = E_g \mp \frac{1}{2} N_0(\alpha - \beta) x < S_z > \mp \frac{1}{2} |3g_h - g_e| \mu_B H + \sigma H^2, \qquad (3)$$

where g_h and g_e are the g-values of the hole and electron, respectively. In eq.(3) the second term is the contribution of the sp-d interaction, the third term is the linear Zeeman splitting of the exciton, and the fourth term is the diamagnetic shift of the exciton, where σ is its coefficient.

IV. Magnetoabsorption Spectra

Figure 4 shows the magnetoabsorption spectra of $Cd_{1-x}Mn_xSe$(x=0.38) in H//c with the π polarization. The absorption edge shifts to lower energies with increasing magnetic field, and an additional line A' appears near the absorption edge. The A' line was distinguished in the fields higher than 0.25 T. The energy shift of the A' line is larger than that of the absorption edge, and it is plotted versus magnetic field in Fig.5.

In the π polarization only the B exciton transition is allowed, as shown in Fig.3. Thus, the observed absorption edge is assigned to the B exciton transition. However, the A' line cannot be considered to be the B exciton transition, because the energy shift of the A' line is not the same as that of the absorption edge. The energy shift of the A' line can be reproduced by the calculation of the A exciton

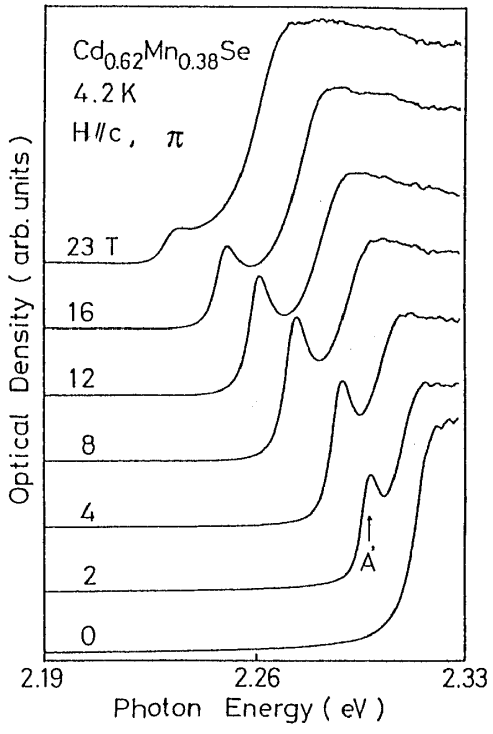

Fig.4. Magnetoabsorption spectra of $Cd_{1-x}Mn_xSe$ (x=0.38).

energy, as described below. Moreover, we found that the A' line has lower energy than the absorption edge at σ polarization, which is assigned to the A exciton transition. Consequently, we attribute the A' line to the transition to an impurity level associated with the A exciton.

The energy of the σ^+ transition was calculated by eq.(3) using $|3g_h-g_e|=1.76$ and $\sigma=1.28\times10^{-5}$ eV/T, which are evaluated in CdSe. The $<S_z>$ value was estimated from the magnetization measurements. The calculated curves are drawn by the solid line in Fig.5, and the fitting parameter is $N_0(\alpha-\beta)=1.28\pm0.05$ eV, which is consistent with the results of magnetoreflectance spectra by Aggarwal et al.[3] The broken lines in Fig.5 denote the calculations without the last two terms in eq.(3). It can be seen that the shift to lower energy is mainly caused by the sp-d interaction, and that the last two terms in eq.(3) cannot be neglected in the high magnetic fields.

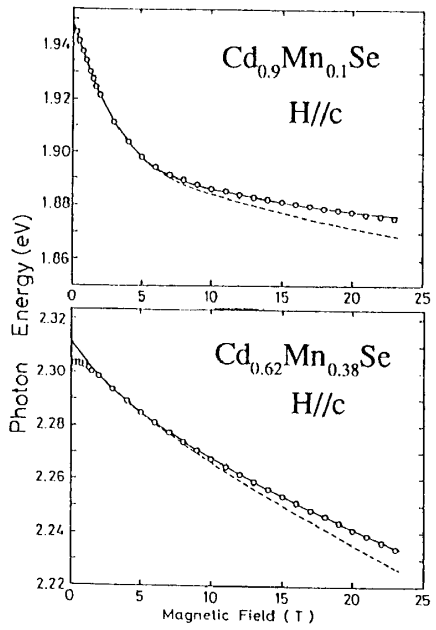

Fig.5. Energy plots of the A' line vs magnetic field for $Cd_{1-x}Mn_xSe$ (x=0.10 and 0.38). The solid lines are calculated from eq.(3) and the broken lines show the contribution from the sp-d exchange interaction.

V. Magnetoluminescence Spectra

The magnetoluminescence spectra of $Cd_{1-x}Mn_xSe$(x=0.10) in H//c are shown in Fig.6. A broad line L1 and a shoulder L2 on the high energy side of L1 are observed in the absence of magnetic field. The L2 shoulder grows into a peak with increasing magnetic field, whereas the L1 line decreases in intensity and disappears above 5 T. In addition, an extra line L3 is seen above 2 T.

The L1 and L2 lines have been also observed in $Cd_{1-x}Mn_xSe$(x=0.05) by Heiman et al.[4] and assigned to the donor-bound A exciton recombination and the free A exciton recombination, respectively. According to their explanation, the striking change in intensity of both lines is attributed to a field-induced instability of the binding to the impurity, re-

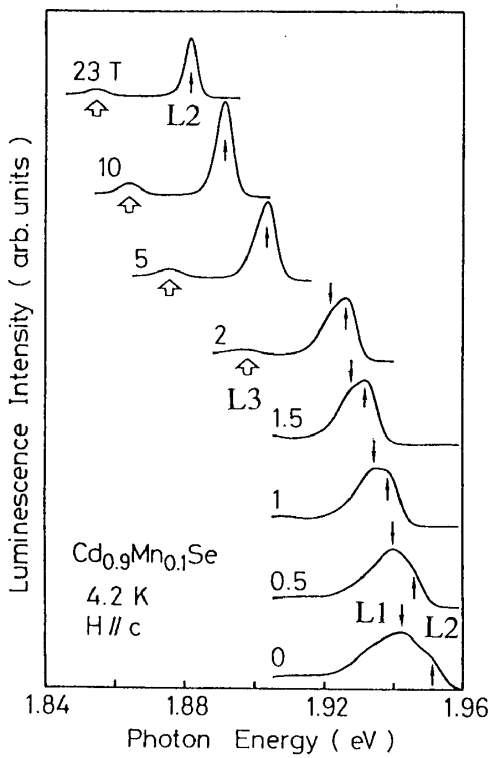

Fig.6. Magnetoluminescence spectra of $Cd_{1-x}Mn_xSe$ (x=0.10).

sulting from the exchange interaction and the Pauli exclusion.

The energies of luminescence peaks are plotted against magnetic field in Fig.6. The solid lines are calculated from eq.(3) for the σ^+ A exciton transition using the same parameters as given above. It can be seen that the energy shift of the L3 line is reproduced by eq.(3). This indicates that L3 lines is the recombination of the A exciton trapped at the deeper impurity level.

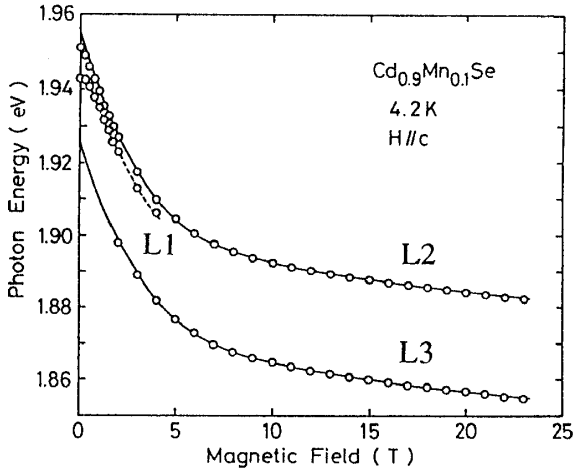

Fig.7. Energy plots of the luminescence peaks vs magnetic field for $Cd_{1-x}Mn_xSe$ (x=0.10). The solid lines are calculated from eq.(3).

VI. Magnetoreflectance Spectra

Figure 8 shows the magnetoreflectance spectra of the A exciton in $Cd_{1-x}Co_xSe$ (x=0.012) in H//c. The A exciton transition splits into two branches with different polarizations (σ^+ and σ^-) in the magnetic fields. The energies of two branches are plotted against magnetic field in Fig.9. The splitting rapidly increases with increasing magnetic field up to approximately 8 T. In the field higher than 12 T, where the magnetization is saturated,[7] the slight increase of the splitting can be seen and both branches shift to higher energies with increasing field.

The splitting energy of the A exciton is written as

$$\Delta E_{A\sigma} = N_0(\alpha - \beta)x < S_z > + |3g_h - g_e|\mu_B H. \quad (4)$$

Figure 10 shows the observed splitting energies (open circles) and the fitting curve to eq.(4) (solid line), where the $<S_z>$ value was estimated from the magnetization measurements and we employed $|3g_h-g_e|=1.76$, assuming that the g-values of the hole and the electron are independent of the x value in small x region. From this fit we evaluated $N_0(\alpha-\beta)=2.52$ eV, which is somewhat larger

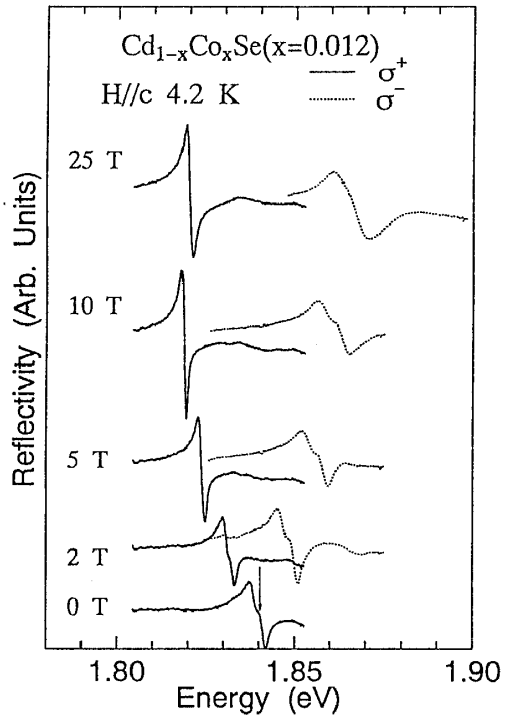

Fig.8. Circularly polarized magnetoreflectance spectra of $Cd_{1-x}Co_xSe$ (x=0.012).

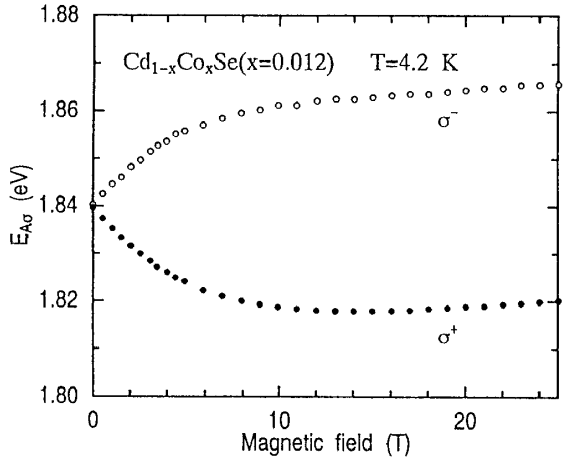

Fig.9. Transition energies of the A exciton vs magnetic field for $Cd_{1-x}Co_xSe$ (x=0.012). The transition energy value of each structure was taken at the midpoint of its negative slope portion indicated by the arrow in Fig.8.

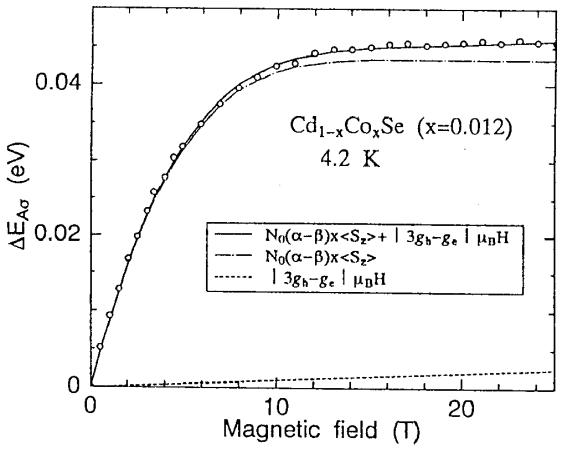

Fig.10. The energy splitting of the A exciton vs magnetic field. The dashed-and-dotted , broken and solid lines represent contribution of the sp-d exchange interaction, the linear Zeeman splitting and their combination, respectively.

than that of Hamadani et al.[8] (2.162 eV). It is possibly due to the overestimation of the x value in their experiment.

The diamagnetic shift of the A exciton was estimated from the averaged energy of two branches and its coefficient σ was evaluated as $\sigma=6.8\times10^{-6}$ ev/T^2, which is smaller than that of CdSe 1.28×10^{-5} eV/T^2.[9] This probably results from the increase of the reduced electron-hole mass and the decrease of the Bohr radius of the exciton in $Cd_{1-x}Co_xSe$.

VII. Summary

The high field magnetooptical measurements of $Cd_{1-x}Mn_xSe$ and $Cd_{1-x}Co_xSe$ have shown that the sp-d exchange interaction leads to the large splitting of the A exciton transition resulting in the striking reduction of the band gap, and that the linear Zeeman splitting and the diamagnetic shift of the exciton can be detected in high magnetic fields, where the magnetization is nearly saturated. The evaluation of the sp-d exchange constant reveals that $N_0(\alpha-\beta)$ in $Cd_{1-x}Co_xSe$ is approximately two times larger than that in $Cd_{1-x}Mn_xSe$; $N_0(\alpha-\beta)=1.28$ eV for $Cd_{1-x}Mn_xSe$ and 2.52 eV for $Cd_{1-x}Co_xSe$, respectively.

Acknowledgments

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